

THE CONSTITUTIONAL FACTOR IN THE
FORMATION OF CERTAIN TRI-
MOLECULAR ORGANIC
COMPLEXES.

THESIS

presented by

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for the degree of Doctor of Philosophy
in the Faculty of Science of the
University of Glasgow.

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May, 1938.

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TO MY PARENTS.

P R E F A C E.

A brief account of some of the work described herein will be found in a paper published by the author jointly with Dr. Kent in the Journal of the Chemical Society, 1938, page 8. A reprint of this paper is included as an appendix to this thesis.

The author wishes to express his deep appreciation of the invaluable advice and assistance so generously given by his supervisor, Dr. Andrew Kent. He also wishes to thank most sincerely Mr. J.M.L. Cameron for carrying out the microanalyses necessary in this investigation.

The author further acknowledges his indebtedness to the University of Glasgow for the tenure of a Donaldson Scholarship and to the Carnegie Trustees for a Research Scholarship during the period in which this work was performed.

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THE CONSTITUTIONAL FACTOR IN THE
FORMATION OF CERTAIN TRI-MOLECULAR
ORGANIC COMPLEXES.

"Mehr und mehr stellt sich in neuerer Zeit heraus, dass das Studium der organischen Molekülverbindungen berufen ist, manches Licht auf die Natur der Absorptionserscheinungen, der Lösungsvorgänge, der enzymatischen Auf- und Abbaureaktionen, der Kristallstrukturen usw. zu werfen."

Paul Pfeiffer.

PART I.

INTRODUCTION.

A. The Formation and General Properties of Polynitro Molecular Compounds.

The first examples of additive complexes formed by aromatic polynitro substances appear to be the picrates of benzene and naphthalene isolated by Fritzsche⁽¹⁾ in 1859. That this property of forming coloured crystalline addition compounds is also possessed by di- and tri-nitro aromatic hydrocarbons was shown by Hepp⁽²⁾ in 1882. Since then the molecular complexes formed between a wide range of aromatic polynitro substances on the one hand, and a variety of aromatic substances on the other* have been prepared and investigated. The value of such derivatives in the isolation and characterisation of aromatic substances is well known; in addition they present interesting and important theoretical problems, especially the question of the mechanism by which their components are linked together.

Although as Hammick, Andrew and Hampson⁽³⁾ show, complexes in which a mononitro substance combines with a di- or tri-nitro substance occur, no substantiated case is

*The two components of such molecular compounds are termed the "nitro" substance or component and the "aromatic" substance or component throughout. Thus in the complex of naphthalene and s-trinitrobenzene², for example, the "nitro" substance is s-trinitrobenzene and the "aromatic" substance is naphthalene.

known in which a mononitro substance acts as the "nitro" component⁽⁴⁾. The m-nitrophenol-anthracene complex reported by Kremann and Müller⁽⁵⁾ may be an exception, but the evidence put forward for its existence is very unsatisfactory. The additive compounds formed between mononitro phenols and amines such as those described by Buehler, Alexander and Stratton⁽⁶⁾ are presumably formed by union between the hydroxyl group of the phenolic component and the amino group of the amine, and are not in the same category as the molecular compounds formed by "nitro" substances. Ortho dinitro compounds appear to be incapable of furnishing crystalline complexes⁽⁵⁾, and it can therefore be said that in the "nitro" component at least two nitro groups situated meta or para to each other are necessary for the formation of crystalline molecular compounds. Trinitro substances combine with a greater range of "aromatic" substances than dinitro substances and yield more stable derivatives⁽⁵⁾.

Considerable variety is shown in the "aromatic" component. Hydroxyl and amino groups in this component promote complex formation, aromatic amines and phenols yielding particularly stable derivatives. Substituents of an acidic nature like -COOH , and $\text{-SO}_3\text{H}$, on the other hand, reduce the tendency to form complexes⁽⁷⁾.

Molecular derivatives of "nitro" substances are generally coloured even though the constituent substances are themselves colourless. The investigations of Sudborough and St. Beard^{(7), (8)}, and Pfeiffer⁽⁹⁾ on the influence of substituents on complex colour show that the effect of any substituent is exactly parallel to the characteristic auxochromic effect which it would exert if substituted in a coloured dyestuff.

Although they generally possess a characteristic congruent melting point, in some cases higher than that of either component, molecular complexes are in many ways unstable. In reasonably dilute solution, as molecular weight determinations show, they are almost entirely dissociated^{(7), (10)}, and even in the fluid state they are dissociated to a considerable extent⁽¹¹⁾. Bamberger and Dimroth⁽¹²⁾ show that solvents in which one component is much more soluble than the other decompose them by dissolving out the more soluble material. Because of this tendency to decompose into their components in solution and in the fluid state, they cannot be said to possess any well-defined chemical properties distinct from those of their constituent substances.

B. Composition of Molecular Compounds of
 Polynitro-substances.

On a statistical survey of some 700 molecular compounds, formed by the union of various "nitro" substances with a variety of "aromatic" substances of widely different constitution, Pfeiffer⁽¹³⁾ found that about 85% contained the two components in equimolecular proportion. A smaller number, about 12%, in which the "aromatic" component usually contained two separate benzene or condensed nuclei, he found to possess 2:1 composition, formed by the union of two molecules of the "nitro" component with one molecule of the dinuclear "aromatic" substance. These figures agree with the view put forward by Bruni⁽¹⁴⁾ in 1906 that normally each molecule of the "nitro" substance can enter into combination with one benzene or condensed nucleus. The great majority of complexes follow this rule and may be regarded as normal complexes.

The remaining 1-2% of the molecular derivatives reviewed by Pfeiffer were according to Bruni's rule abnormal and included a number of derivatives of 1:2 composition in which each molecule of the "nitro" substance was linked to two molecules of the "aromatic" substance. In addition to these ternary derivatives there were a

few isolated cases to which a more complicated structure had been ascribed; of these, however, only the 3:2 derivative of s-trinitrobenzene and fluorene^{(15),(16)} and the 4:5 derivative of s-trinitrobenzene and 2-amino-fluorene⁽¹⁷⁾ can be regarded as authenticated; in the other cases additional evidence appears to be required.

C. Formation of Ternary Complexes.

The first case of a 1:2 molecular compound (i.e., one molecule of the "nitro" component united to two molecules of the "aromatic" component) appears to be the m-dinitrobenzene derivative of tetramethyldiaminodiphenylmethane reported by van Romburgh in 1888⁽¹⁸⁾ (although the proof for its abnormal structure was not given until 1911⁽¹⁹⁾). Among the substances whose molecular compounds with s-trinitrobenzene have been investigated by Sudborough and his co-workers are the following which give ternary 1:2 derivatives:- carbostyryl, dibenzylaniline, α -naphthoic acid⁽¹⁵⁾, "hydroxy-lepidine", 7-hydroxyquinoline, coumarin and fluorenone⁽⁸⁾ (crystalline derivatives were not obtained from the last two substances, the ternary complex being shown by a maximum at this composition on the melting point curve of the components). m-Cresol⁽²⁰⁾ and α -methyl- β -phenyl naphthalene⁽²¹⁾ both yield crystalline picrates of ternary composition, and Hammick, Hill and Howard⁽²²⁾, on

the evidence of a melting point curve postulate a 1:2-s-trinitrobenzene derivative for benzene itself. Recently Kent⁽²³⁾ has shown that 1-keto-1:2:3:4 tetrahydrocarbazole not only gives ternary derivatives with s-trinitrobenzene and picric acid, but also with m-dinitrobenzene, p-dinitrobenzene, 2:5-dinitrotoluene and 2:4:5-trinitrotoluene.

Such 1:2 compounds can be accounted for in a number of ways:-

(1) As Bennet and Wain⁽²⁴⁾ have already suggested for certain derivatives of anomalous constitution formed by cyclic oxides and phenols (such as the 1:2 derivative of β -naphthol and tetramethylphthalan), they may arise from the action of some secondary influence like crystalline convenience. On this basis only one molecule of the "aromatic" component can be regarded as bound to the "nitro" substance, the other being merely held in association with the binary complex by the crystal-lattice forces.

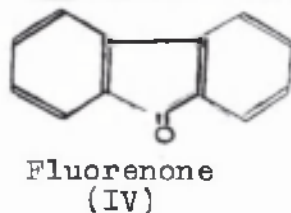
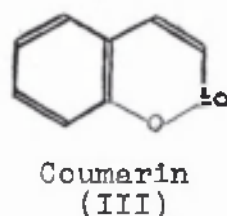
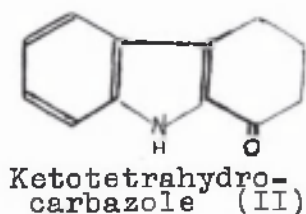
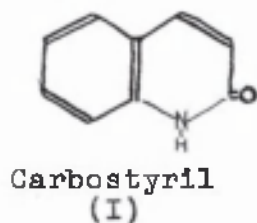
(2) 2:3-dimethyl-pyrrole yields a derivative with picric acid which is apparently of ternary structure but is actually a binary complex of a dimeric form of the "aromatic" component, since, on removal of the picric acid, the corresponding dipyrrole is obtained⁽²⁵⁾. Although none of the substances which yield ternary derivatives mentioned above are known to polymerise in the same manner as the dimethyl-pyrrole, the possibility that

molecular compounds of 1:2 constitution arise from prior association of the "aromatic" component in solution cannot be disregarded. There is no evidence in favour of this view. On the contrary, in the light of the results obtained by Kent⁽²³⁾ it appears improbable.

(3) They may be systematic in their origin and so characteristic of components possessing the requisite chemical (and spatial?) configuration.

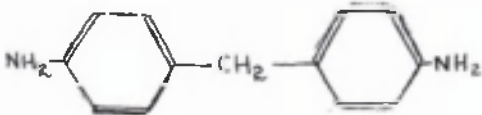
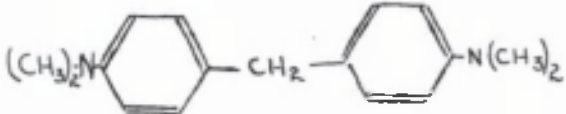

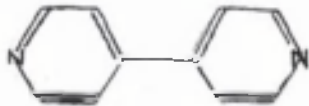

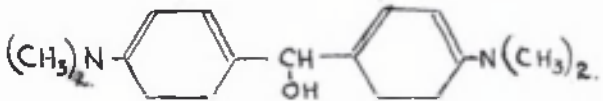
The following facts seemed to point to (3) as most probably the correct explanation of the formation of ternary molecular compounds:

(a) A number of the substances which yield 1:2 complexes possess allied chemical structures.



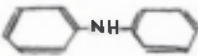
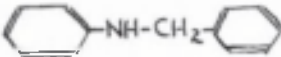
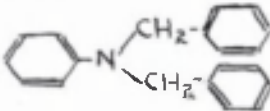
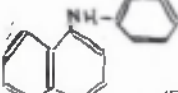
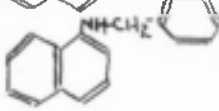
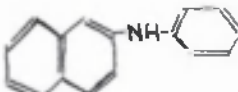
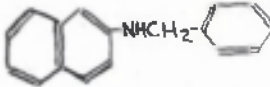
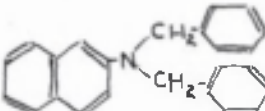
All possess a cinnamonyl grouping. Also (I) is a hydroxy derivative of quinoline, two other hydroxy derivatives of which, 7-hydroxy quinoline and "hydroxyepidine" also give 1:2 s-trinitrobenzene derivatives.

(b) The formation of 1:1 derivatives of dinuclear aromatic substances, especially when such substances possess a symmetrical molecule may be regarded as analogous to the formation of 1:2 derivatives by mononuclear substances. It is noticeable that p-p' disubstituted dinuclear substances frequently yield such irregular 1:1 compounds, e.g., the following substances give 1:1 derivatives with s-trinitrobenzene:

	<u>Ref.</u> 7.
	7.
	26.
	7.
	7.
	7.

(c) The introduction of a benzyl group ($-\text{CH}_2-\text{C}_6\text{H}_5$) is frequently accompanied by a change in complex constitution. Compare the s-trinitrobenzene

derivatives of the substances given in the table below.

Substance.	Composition of sT.N.B. derivative.	Ref.
	Normal 2:1	26
	Abnormal 1:1	7
	Abnormal 1:2	7
	Normal 2:1	7
	Abnormal 1:1	7
	Normal 2:1 and Abnormal 1:1	7
	Abnormal 1:1	7
	Abnormal 1:1	7

(d) Of the nine different "nitro" substances whose complexes with ketotetrahydrocarbazole were investigated by Kent⁽²³⁾, five yielded 1:2 derivatives. The

proportion of 1:2 complexes, 55%, found ⁱⁿ this constitutionally restricted field, when contrasted with 1-2% found by Pfeiffer in his general survey, is apparently much too great to be accounted for by accidental influences. The arbitrary choice of "nitro" components renders these results inconclusive; it remains possible, though unlikely, that the five "nitro" substances, from which Kent obtained 1:2 derivatives with ketotetrahydrocarbazole are the only ones which behave thus in the considerable range of possible "nitro" components.

D. Objects and Methods of this Investigation.

On the basis of the evidence given in the previous section, it appeared to be a reasonable possibility that the 1:2 additive complexes formed by "nitro" substances are systematic in their origin and manifest in their abnormal constitution some property possessed only by members of a very restricted group of "aromatic" components. To establish this view was the primary object of this work, and it was hoped that the results obtained would throw some light on the mode of formation of these abnormal compounds. So far no adequate explanation of the mechanism by which "nitro" substances are able to unite with aromatic substances has been possible on the

results of the considerable amount of research already done on molecular compounds of polynitro substances. Such research however has been almost solely devoted to the more common normal 1:1 and 2:1 types. The hope that the results obtained from a systematic study of 1:2 complexes, which constitute a small distinct group, differing from the normal 1:1 and 2:1 types only in their irregular composition, might prove of value towards a complete elucidation of the mechanism binding the components in molecular compounds of polynitro substances was therefore an additional consideration which prompted this work.

If the idea that the formation of ternary addition complexes is a function of the chemical nature of their components is correct, then it would be expected that derivatives of those substances which yield such abnormal complexes would retain to some degree this property of their parent substance. The conversion of carbostyryl⁽¹⁵⁾ to quinoline^{(7), (26)}, of ketotetrahydrocarbazole to tetrahydrocarbazole⁽²³⁾, the change from 7-hydroxy- to 8-hydroxyquinoline⁽⁸⁾, and of benzene (Hammick, Hill and Howard⁽²¹⁾ vice Fritzsche⁽¹⁾) to toluene⁽²⁷⁾ all destroy the power to give 1:2 molecular derivatives. It is obvious therefore that the range within which structural alteration might be expected to maintain this property is a very limited one, and that the investigation of derivatives whose formation has involved anything like a major structural

alteration will yield results incapable of interpretation.

Always excepting of course the substitution of deuterium for hydrogen (which could not be accomplished systematically in this work), the slightest possible modification of an organic compound is the replacement of a methyl group for a hydrogen atom. If such monomethylation should destroy the power to yield 1:2 complexes, then any constitutional factor involved in the formation of these substances is too slight (as in the case of benzene compared with toluene [vide supra] , and *s*-trinitrobenzene compared to *s*-trinitrotoluene⁽²³⁾) to be capable of chemical demonstration. Prior to this work no evidence was available that monomethyl derivatives of "aromatic" components retain the property of their parent substance to give 1:2 complexes, although it appeared not unlikely that Sudborough's "hydroxylepidine"⁽⁸⁾ was in fact 4-methylcarbostryl, and therefore a methyl derivative of a substance capable of forming 1:2 addition compounds. With regard to the effect of methylating the "nitro" component, the evidence⁽²³⁾ was inconclusive.

In view of the fact that comparatively slight alteration in structure has been found to be capable of destroying the property of yielding ternary derivatives and the fact that the influence of secondary factors like crystalline convenience, steric effects, disparity in component solubility, etc. may at times be considerable,

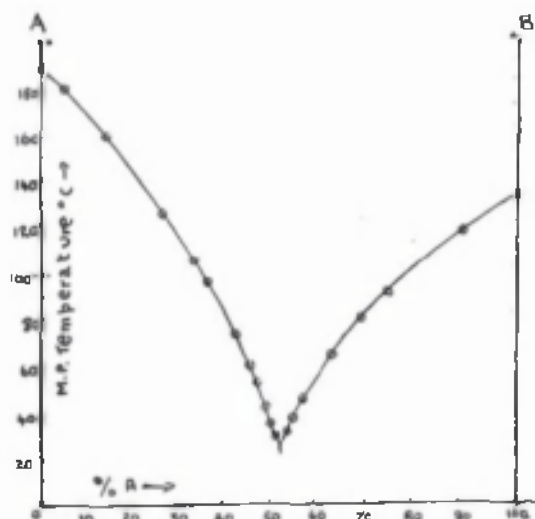
the best approach to this problem is a statistical one. It was therefore proposed to prepare all the relevant monomethyl derivatives of certain substances known to be capable of forming ternary complexes and consider the molecular compounds formed by such derivatives, with selected "nitro" components, as a group.

Obviously the first series of "aromatic" components to be investigated were the monomethyl derivatives of ketotetrahydrocarbazole which yields stable, easily formed molecular compounds with a variety of "nitro" substances, several of which are ternary. Also all the possible C-methyl derivatives of ketotetrahydrocarbazole are, at least theoretically, accessible by synthesis, an important factor in the choice of this series as "aromatic" components. The second series of "aromatic" components chosen was the dibenzyl-toluidines which were regarded as the relevant monomethyl derivatives of dibenzyl aniline and which were all readily accessible. The C-methyl derivatives of carbostyryl, which are all obtainable by synthetic methods although in some cases with difficulty, were also investigated; the parent substance gives a stable ternary complex with s-trinitrobenzene⁽¹⁵⁾.

The "nitro" substance whose molecular complexes with these selected "aromatic" components were investigated

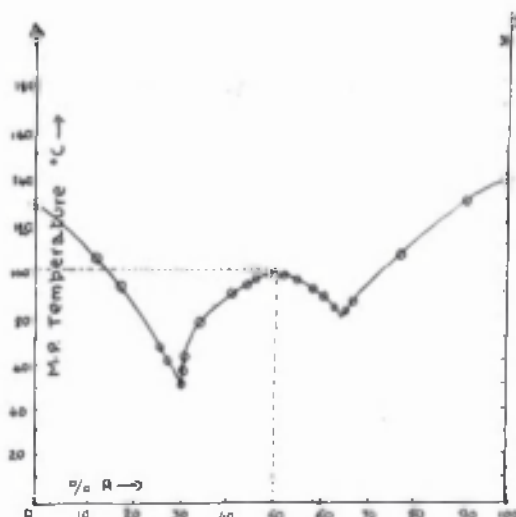
was s-trinitrobenzene. This "nitro" component was chosen because it was known to yield the greatest range of stable additive derivatives, and also because the three substances from which the "aromatic" components were derived gave ternary s-trinitrobenzene compounds. Tetramethyldiaminodiphenylmethane, although giving a binary complex with s-trinitrobenzene⁽⁷⁾, yields a ternary complex with m-dinitrobenzene⁽¹⁹⁾. With the exception of the supposed ternary picrates of anthranilic acid, p-toluidine and (β -naphthyl amine reported by Suida⁽²⁸⁾ (which cannot be accepted without further and stronger evidence), this is the only case known in which an "aromatic" substance displayed its power to yield ternary derivatives towards a "nitro" substance other than s-trinitrobenzene. In this research, therefore, those "aromatic" components which failed to yield 1:2 complexes with s-trinitrobenzene were always investigated with regard to their behaviour towards m-dinitrobenzene. Because of their value for characterisation purposes, picrates were also prepared and investigated. Since the "aromatic" substances used were basic in character picrates of salt-like character⁽²⁹⁾, not analogous to the corresponding molecular s-trinitrobenzene derivative, were to be expected, except in the case of the methyl derivatives of ketotetrahydrocarbazole which itself yields a ternary molecular picrate.

There are two possible ways of determining the composition and melting point of an addition complex. There is first the method of thermal analysis extensively used by Kremann who maintains ⁽³⁰⁾ that this method is the only satisfactory one for proving the existence or non-existence of a complex. In this method the melting points of mixtures of the components are plotted against their percentage compositions, and the resultant curve examined. A simple eutectic curve (Fig.1) denotes that no complex is formed; a curve of the form shown in Fig.2 indicates complex formation, the composition and melting point of the complex being given by the maximum on the graph.



Graph indicating non-formation of complex.

Fig.I.



Graph indicating the formation of a 1:1 complex, m.p. 100°.

Fig.II.

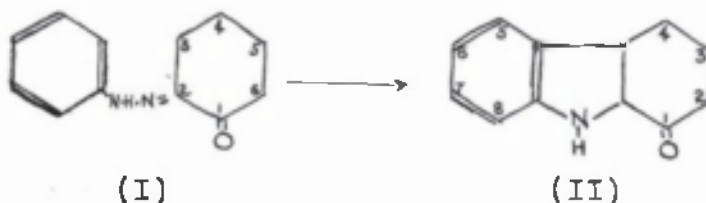
The other method is to isolate the crystalline complex from a suitable solvent and submit it to the usual chemical analysis. Bamberger and Dimroth⁽¹²⁾ have worked out the conditions for the isolation of crystalline binary complexes and state that it is possible to isolate complexes, whose existence is not shown on a thermal analysis diagram, from a solution containing the components in suitable concentration. This second method was chosen for the work described here. In certain cases where no crystalline derivative could be isolated, melting point curves were examined.

PART II. PRACTICAL.

Section A. Preparation of derivatives of 1-keto-
1:2:3:4-tetrahydrocarbazole.

1. General description of methods employed.

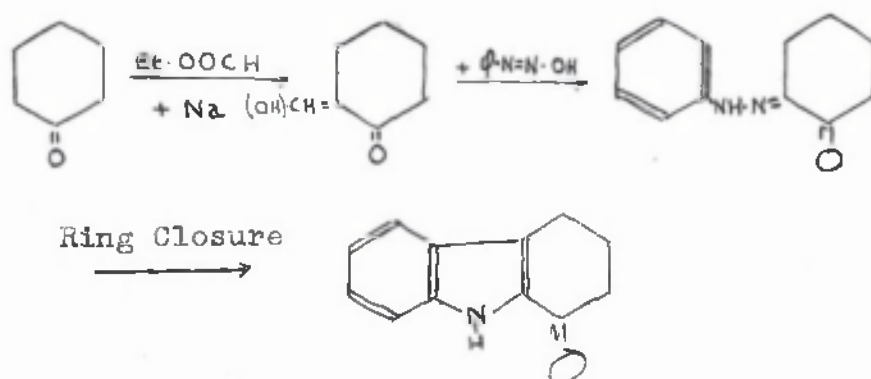
The required derivatives of keto-tetrahydrocarbazole (II) were obtained from the corresponding derivatives of cyclohexane-1:2-dione-monophenyl-hydrazone (I) which, as first demonstrated by Borsche⁽³¹⁾ readily undergoes ring closure when boiled with dilute mineral acids.



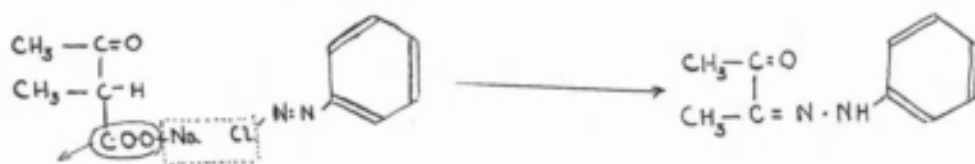
There are two accessible routes to these required intermediates.

(a) Bishop, Sinclair, and Claissen⁽³²⁾ in their exhaustive study of hydroxy methylene camphor, showed that it reacts with benzene diazonium hydroxide to give the mono-phenylhydrazone of camphor quinone. Coffey⁽³³⁾ applied this reaction to the preparation of cyclohexane-1:2-dione-monophenyl-hydrazone by coupling hydroxy-methylene-cyclohexanone (prepared from cyclohexanone, benzyl formate and sodium wire by the original method of

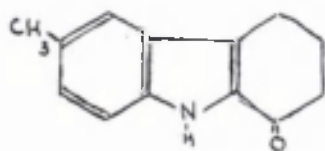
Wallach⁽³⁴⁾, with a solution of benzene diazonium hydroxide. Using this method Sen and Ghosh⁽³⁵⁾ prepared cyclohexane-1:2-dione-mono-p-tolylhydrazone and 6-methyl-cyclohexane-1:2-dione-2-phenylhydrazone, which they converted to 1-keto-6-methyl- and 1-keto-2-methyl-tetrahydrocarbazoles respectively. Mears, Oakeshott and Plant⁽³⁶⁾ found ethyl formate to be superior to amyl formate for the preparation of the hydroxy methylene derivatives of the cyclic ketones; they describe the preparation of the 6-methyl and 8-methyl derivatives of ketotetrahydrocarbazole. This first method may be formulated thus:-



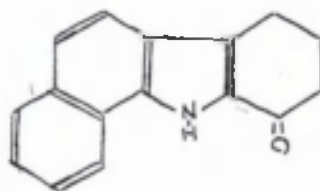
(b) The second method was based on a reaction of Japp and Klingemann⁽³⁷⁾ who showed that when the sodium salts of α -monosubstituted- β -ketonic acids were treated with a solution of benzene diazonium chloride there was obtained mono-phenylhydrazones of diketones thus:-



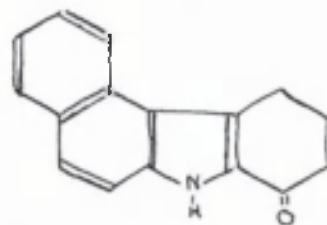
Dieckmann⁽³⁸⁾ applied this reaction to cyclic- β -ketonic acids, and by treating the sodium salt of cyclopentanone-2-carboxylic acid with benzene diazonium chloride obtained cyclopentane-1:2-dione mono phenyl hydrazone. Using the sodium salt of cyclohexanone-2-carboxylic acid and a number of diazotised amines, Lions⁽³⁹⁾ prepared among other derivatives the mono-*p*-tolylhydrazone, and the mono- α - and - β -naphthylhydrazones of cyclohexan 1:2 dione. These he converted into (III), (IV) and (V).



(III) 6-methyl-keto-tetrahydrocarbazole

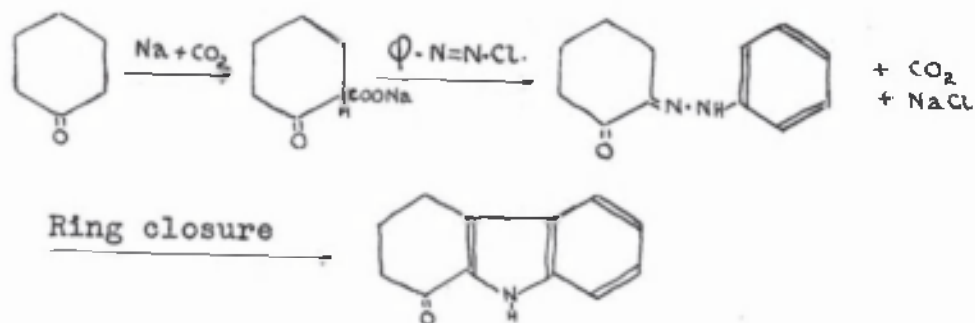


(IV) 7-8-benzoketotetrahydrocarbazole



(V) 5-6-benzoketotetrahydrocarbazoles.

This second method may be formulated thus:-



The preparation of the complete series of mono-methyl derivatives of 1-keto-1:2:3:4-tetrahydrocarbazole thus involved the synthesis of four hitherto unknown derivatives. (IV) and (V) were also prepared and their behaviour towards *s*-Trinitrobenzene and Picric acid investigated.

2. Preparation of the necessary phenylhydrazones.

4-Methyl-cyclohexane-1:2-dione-2-mono-phenylhydrazone was prepared by each of the two methods given; the following detailed description of the synthesis of this new substance by each method will serve to show the typical experimental procedure involved.

Preparation of 4-methyl cyclohexane-1:2-dione-2-phenylhydrazone by Method (a).

4-Methyl-cyclohexanone (obtained from Poulenc Frères) was first purified through its bisulphite compound, which was obtained as a colourless crystalline substance by shaking with a concentrated solution of sodium bisulphite. This substance, after purification,

was decomposed by heating with excess sodium carbonate solution on the water-bath, the regenerated ketone was extracted with ether, the ether removed and the residue distilled.

7.5 g. of this purified 4-methyl cyclohexanone along with ethyl formate (8 g.) were placed in a wide-mouthed, stout walled bottle, and sodium (2 g.) atomised under toluene, was added in small portions, the temperature being kept below 5°C. throughout. A white solid was formed and towards the end of the reaction the contents of the bottle became almost completely solid, and, to ensure that the last portions of sodium react, they were pounded vigorously with a glass rod. When all the sodium had been added the bottle was placed in the refrigerator (it may be kept thus for several days without decomposition).

Aniline (5 g.) was diazotised in the usual manner, and this diazo solution, after neutralising by adding excess sodium acetate, was diluted with ice-water (150 c.c.).

Meanwhile the contents of the bottle were dissolved in ice water, and the resultant opaque yellow solution, after extraction with carbon tetrachloride to remove unchanged starting products, was neutralised with acetic acid. The suspension of 2-hydroxymethylene-4-methyl cyclohexanone thus obtained was made up to 300 c.c. with ice-water and added to the diluted, neutralised diazo

solution with vigorous stirring.

When the two solutions were mixed a red oil separated which on stirring solidified to a yellow solid (5 g.). After recrystallisation from alcohol, it was obtained as light yellow plates, m.p. 140° . (Found: N, 13.0. $C_{13}H_{16}ON_2$ requires N, 12.96%).

By method (b).

4-Methyl-cyclohexanone, purified as described in previous method, was converted to 2-carboxy-4-methyl-cyclohexanone by the method of Gardner, Perkin and Watson⁽⁴⁰⁾. This consisted in adding the 4-methyl-cyclohexanone (28 g.) dissolved in petroleum ether (75 c.c.) to powdered sodamide (10 g.) under petroleum ether in a moisture-free apparatus fitted with a stirrer. Ammonia was evolved, and the white sodium derivative of the ketone was deposited. When the ammonia evolution ceased, a rapid stream of carbon dioxide was passed through the reaction mixture, which was vigorously stirred. At the end of the reaction ice was added to dissolve the sodium salt of the 4-methyl-cyclohexanone-2-carboxylic acid which is formed during the reaction. The aqueous layer was separated, neutralised with dilute hydrochloric acid and cooled, when the desired acid crystallised out although in very poor yield (3 g.).

1.5 g. of this acid was dissolved in 20 c.c. water containing NaOH (1 g.) and this solution left in the refrigerator while a solution of benzene diazonium chloride was prepared by diazotising aniline (1.8 g.) and adding to excess sodium acetate in ice-water (80 c.c.). This diluted diazo solution was then added to the solution of sodium 4-methyl-cyclohexanone-2-carboxylate which had been diluted with a like quantity of ice-water, and the whole vigorously stirred. CO_2 was evolved, and a red brown solid separated, which was filtered off and recrystallised from alcohol. Yield 1.5 g. as small rectangular salmon pink plates, m.p. $139 - 139.5^\circ$ (Found: N, 13.11%).

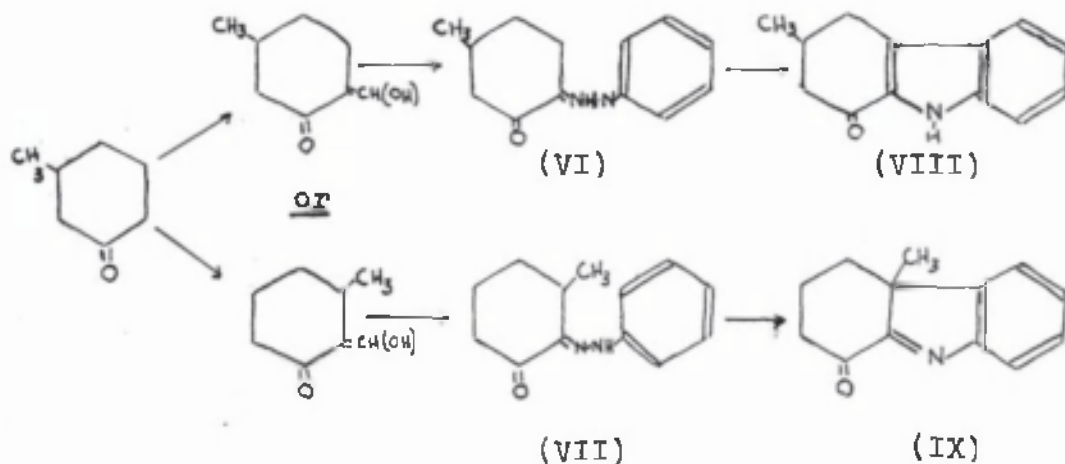
Although differing in appearance from the 4-methyl-cyclohexane-1:2-dione-2-phenylhydrazone prepared by the first method, this substance had the same melting point, and a mixed melting point was $139 - 140^\circ$. Moreover both specimens yielded identical products on indolisation. No evidence of stereoisomerism was observed.

For the preparation of the other hydrazones described below method (a) was used, the poor yield obtained from the first stage of method (b) rendering this method uneconomical.

When 3-methyl-cyclohexanone (b.p. $169 - 170^\circ$ /737 m.m.) was treated with ethyl formate and atomised

sodium, a brown semi-fluid paste was obtained. This differed from the other preparations in which a solid sodium derivative of the hydroxymethylene compound was obtained. When this paste was condensed with the diazo solution, a scarlet solid was obtained in good yield. This recrystallised from alcohol as a red-brown crystalline solid, which sintered at 165° , softened at 194° and melted $197 - 203^{\circ}$. Two further crystallisations from alcohol did not affect the melting point. (Found: N, 13.12%). This substance was sparingly soluble in organic solvents, behaving in this respect like the other hydrazones prepared.

The treatment of the hydroxy-methylene compound of 3-methyl-cyclohexanone with diazotised aniline can give rise to two isomeric phenyl hydrazones, (VI) and (VII) thus:-



(VI) on indolisation would yield 1-keto-3-methyl-1:2-tetrahydrocarbazole (VIII), whereas (VII) under the influence of indolising media might either hydrolyse to phenyl-hydrazone and 3-methyl-cyclohexanone or give the indolenine (IX) by ring closure.

The red brown solid obtained, on indolisation yields a homogeneous substance, m.p. $194 - 195^{\circ}$ in 70% yield, which is only 10% less than normal. This substance yields a ternary molecular picrate (p. 67) analogous to the picrates of ketotetrahydrocarbazole and certain of its methyl derivatives, and incompatible in properties with the salt-like picrates obtained from indolenines (cf. Plancher⁽⁴¹⁾). The substance obtained on indolisation is therefore evidently (VIII) and the yield obtained indicates that the substance present with (VI) occurs in relatively small amount and is removed by indolisation.

Cyclohexane-1:2-dione-mono-m-tolylhydrazone obtained by method (a) from cyclohexanone and m-toluidine, crystallises from alcohol as light brown plates, m.p. $156 - 158^{\circ}$. (Found N, 13.1%). This substance has not hitherto been described.

6-Methyl-cyclohexane-1:2-dione-2-phenyl-hydrazone prepared from 2-methyl cyclohexanone and aniline was obtained from methyl alcohol as light yellow prisms,

m.p. 97.5 - 98°. (Found: N, 13.1%). The product obtained in a similar manner by Sen and Ghosh⁽³⁵⁾ is reported by these workers to be a mixture of two isomers melting from 91 - 131°, with sintering at 88°. I found no confirmation for these statements; the substance obtained being homogeneous, of sharp melting-point, and yielding on indolisation an 80% yield of the corresponding 2-methyl ketotetrahydrocarbazole identical in melting point with that obtained by Sen and Ghosh from their product.

Cyclohexan-1:2-dione-mono-o-tolyl-hydrazone, prepared from cyclohexanone and o-toluidine, crystallised from alcohol as red prisms, m.p. 95 - 96°. This substance has been already prepared and described by Mears, Oakeshott and Plant⁽³⁶⁾.

Cyclohexan-1:2-dione-mono-p-tolyl-hydrazone, prepared by method (a), was obtained from alcohol as orange plates, m.p. 137 - 139°. It has been previously prepared by Sen and Ghosh⁽³⁵⁾, Mears, Oakeshott and Plant⁽³⁶⁾, and Lions⁽³⁹⁾.

Cyclohexan-1:2-dione-mono- α -naphthyl-hydrazone was obtained by method (a), and crystallised in brown plates (from alcohol), m.p. 133°.

Cyclohexan-1:2-dione-mono-(β -naphthyl-hydrazone was obtained in 65% yield by method (a). It crystallised from alcohol as light brown plates, m.p. 173°.

Lions⁽³⁹⁾ has prepared both of these naphthyl hydrazones by method (b).

3. Conversion of the hydrazones to derivatives of
1-keto-1:2:3:4-tetrahydro-carbazole.

In all cases ring closure was effected by the method described by Kent⁽⁴³⁾. The following is a detailed description of a typical indolisation.

4-methyl-cyclohexane-1:2-dione-2-phenyl-hydrazone (1 g.) was dissolved by boiling in glacial acetic acid (10 c.c.). The burner was removed and to the hot solution concentrated hydrochloric acid (1 c.c.) was added drop by drop. Each drop caused a brisk ebullition and the liquid darkened considerably. After all the hydrochloric acid had been added, the solution was boiled for 2 minutes and then boiling water was added until a slight turbidity was produced. On allowing the solution to cool the desired 1-keto-4-methyl-tetrahydrocarbazole crystallised out as brownish coloured crystals, m.p. 125 - 128°, which on crystallisation from alcohol were obtained as colourless plates, m.p. 131°. (Found: N, 7.1. $C_{13}H_{13}ON$ requires 7.0%).

No boiling water was necessary to precipitate the benzo-ketotetrahydrocarbazoles (IV) and (V), which crystallised from the acetic acid solution on cooling.

The derivatives of ketotetrahydrocarbazole obtained thus are given below. In certain cases p-nitro-phenylhydrazones were prepared for characterisation purposes, and to see whether they would give contrasted coloured compounds on crystallisation from alcohol as the p-nitrophenylhydrazone of the parent ketotetrahydrocarbazole does⁽²³⁾. The references are to previous preparations and descriptions of these substances.

The p-nitro-phenylhydrazone of 1-keto-4-methyl-tetrahydrocarbazole was obtained from alcohol as dark red prisms, m.p. 227 - 229° (darkening). (Found: N, 16.9%. $C_{19}H_{18}O_2N_4$ requires 16.8%).

1-Keto-2-methyl-tetrahydrocarbazole was obtained as colourless plates from alcohol, m.p. 172°. (Sen and Ghosh⁽³⁵⁾).

The p-nitrophenylhydrazone crystallised from alcohol as brick red prisms, m.p. 226 - 228°. (Found: N, 16.9%).

1-Keto-6-methyl-tetrahydrocarbazole was obtained from alcohol as colourless needles, m.p. 194-196°. (Sen and Ghosh⁽³⁵⁾; Lions⁽³⁹⁾; and Mears, Cakeshott and Plant⁽³⁶⁾).

1-Keto-8-methyl-tetrahydrocarbazole was obtained from alcohol as colourless needles, m.p. 167°. (Mears, Cakeshott and Plant⁽³⁶⁾).

1-Keto-5:6-benzotetrahydrocarbazole was given as faintly yellow plates from alcohol, m.p. 203-204° (Lions⁽³⁹⁾).

1-Keto-7:8-benzotetrahydrocarbazole was obtained as faintly yellow plates from alcohol, m.p. 239-240° (Lions⁽³⁹⁾).

1-Keto-3-methyl-tetrahydrocarbazole was obtained in 70% yield by indolising the product formed by condensing the hydroxy-methylene compound of 3-methyl-cyclohexanone and diazotised aniline (p.23). Analysis (Found: N, 7.1%) and the nature of its picrate (p. 67) confirm its structure (see p. 25). It crystallises from acetone as yellowish flat needles, m.p. 194-195°. Its p-nitrophenylhydrazone was obtained from alcohol as purple prismatic needles, m.p. 265-267° (darkening). (Found: N, 17.0%).

The 3-methyl- and 4-methyl-derivatives of keto-tetrahydrocarbazoles have not previously been reported.

4. Isolation of 5 (or 7)-methyl- and 7 (or 5)-methyl-ketotetrahydrocarbazoles.

Ring closure of cyclohexane-1:2-dione-mono-m-phenylhydrazone can take place in two positions giving rise to the two isomeric 7-methyl- and 5-methyl-ketotetrahydrocarbazoles, and indolisation in the manner described (p. 27) yielded a mixture of these isomers which melted from 140-190°. (Found: N, 7.1%). If, however, instead of adding hot water until turbidity was produced, successive small quantities of boiling water were added: one of the isomers

was obtained in a relatively pure state thus:-

Cyclohexane-1:2-dione mono-m-tolylhydrazone (7 g.) was dissolved in acetic acid (42 c.c.) and to this boiling solution 7 c.c. concentrated hydrochloric acid were added drop by drop. The resultant dark brown solution was treated with successive small quantities of boiling water (10 c.c. in all) until on cooling a solid crystallised out. This solid (1 g.) was immediately filtered off, and was obtained by recrystallising from alcohol as slightly brownish coloured plates, m.p. 196° . (Found: N, 7.2%). The residual solids, obtained from the filtrate by diluting with a considerable amount of water melted from 125° to 140° ; (Found: N, 7.2%) and attempts to separate this material by fractional crystallisation from alcohol, acetone, or acetic acid were unsuccessful.

According to Borsche, Witte and Bothe⁽³¹⁾, ring closure of a meta substituted phenylhydrazone takes place normally in a position para rather than ortho to the substituent. Although exceptions to this are known⁽⁴²⁾, the isomer obtained as described, which was evidently produced in the greater amount, was assumed to be the 7-methyl derivative rather than the 5-methyl derivative, and will be referred to as 1-keto-7 (or 5)-methyl-tetrahydrocarbazole.

A better yield of this substance was obtained thus:-

2 g. of the mixture from indolisation with half

a molecule of picric acid (1.15 g.) were dissolved by boiling in alcohol (150 c.c.). On cooling a picrate crystallised as orange plates, m.p. after recrystallisation from alcohol 179-180°, and a further 0.75 g. of this material was obtained on evaporating the filtrate to 50 c.c. and refrigerating. By decomposing the 1.25 g. of this picrate obtained, by treatment with ammonia, about 0.8 g. pure 1-keto-7 (or 5)-methyl-tetrahydrocarbazole, identical with that obtained in the previous manner, was produced. Further reduction of the filtrate did not yield the picrate of the 5 (or 7)-methyl isomer but gave the "mixed" picrate described on p.69, as deep ruby-red prisms.

The 7 (or 5)-methyl isomer is evidently concentrated to some extent in the first fraction obtained on recrystallising the indolisation product from alcohol, for on treating 10 g. of such material with half a molecular proportion of picric acid, 11.2 g. of the picrate of the 7 (or 5) isomer were obtained in more or less pure condition, before the deep red "mixed" complex appeared.

Although numerous methods have been tried for the isolation of the 5 (or 7)-methyl isomer from the mixture produced by indolising cyclohexane-1:2-dione-monom-phenylhydrazone, a successful standard method is not yet available. On one occasion, however, a small amount of this substance was obtained thus:-

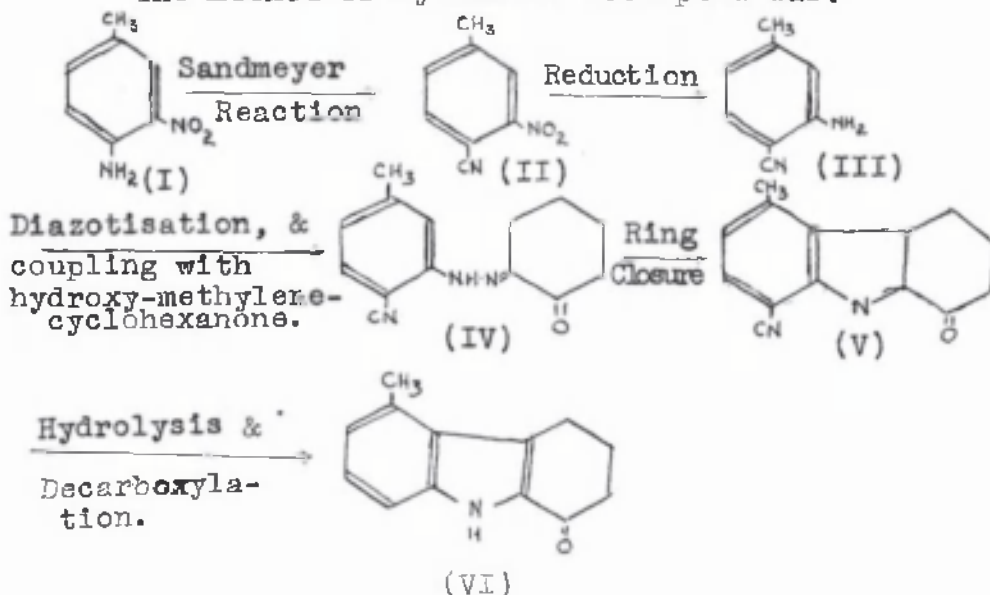
1 g. of the mixture from indolisation was treated with 0.57 g. picric acid in 75 c.c. absolute alcohol, and this solution evaporated by stages, the solid produced on cooling after each evaporation being filtered off. The product from the first few stages was the picrate of the 7 (or 5) isomer. When the solution was reduced to 25 c.c. the picrate precipitated was contaminated to a considerable extent by the deep red "mixed" picrate. The solution (25 c.c.) was then treated with successive small quantities of water, each addition being followed by prolonged refrigeration. Refrigeration overnight after 8 c.c. water had been added resulted in the formation of a small quantity (.1 g.) of colourless prisms, m.p. 160-161° with previous softening. (Found: N, 7.1%). The mixed melting point with the 7 (or 5) isomer was 130-143°. Like ketotetrahydrocarbazole and its methyl derivative this new substance yields ternary complexes with polynitro substances, and can scarcely be other than 1-keto-5(or 7)-methyl-keto-tetrahydrocarbazole.

Although several attempts to repeat this isolation of the 5 (or 7)-methyl derivative have been made, these have so far proved unsuccessful.

Section B. Attempted Synthesis of 1-keto-5-
methyl-tetrahydrocarbazole.

Some time before the isolation of specimens of the isomeric 7 (or 5)-, and 5 (or 7)-methyl derivatives of ketotetrahydrocarbazole described in Section A, subsection 5, an attempt was made to synthesise directly 1-keto-5-methyl-tetrahydrocarbazole. It was hoped that the synthesised substance, about whose structure no ambiguity could exist, would prove different from the isomer obtained in reasonable quantity from the mixture given on indolising cyclohexane 1:2-dione-mono-*m*-tolylhydrazine, and which was assumed to be more probably the 7-methyl derivative than the 5-methyl derivative (p. 30). The direct synthesis of the 5-methyl isomer would in any case enable definite structures to be assigned to the two substances obtained from the indolised mixture.

The method of synthesis attempted was:-



3-Nitro-4-amino-toluene (I) was prepared from p-toluidine as described by Gattermann⁽⁴³⁾

3-Nitro-4-cyano-toluene (II) was obtained from (I) by a Sandmeyer reaction⁽⁴⁴⁾.

3-Amino-4-cyano-toluene (III) was obtained by reduction of (II). This reduction gave rise to some difficulty. The method of Niementowski⁽⁴⁴⁾ gave very poor yields, while reduction with zinc dust in acetic acid saturated with HCl, as described below, was also comparatively unsuccessful.

3-Nitro-4-cyano-toluene (10 g.) was dissolved in glacial acetic acid (130 c.c.) saturated with hydrochloric acid gas, and zinc dust (50 g.) was gradually added. After the addition of about a quarter of the zinc, the colour of the reaction mixture was almost black, later it changed to grey-green. After all the zinc had been added, the reaction mixture was refluxed for two hours, allowed to cool and filtered. After neutralising with ammonia (0.88 Sp. Gr.), the filtrate was extracted with benzene. On evaporating the benzene 2 g. of crude amino-tolunitrile were obtained.

An attempted reduction using stannous chloride in concentrated hydrochloric acid, as described by Bogert and Hand⁽⁴⁵⁾, was completely unsuccessful.

In view of the poor results from these experiments, an attempt was made to hydrolyse the nitrotolunitrile to the corresponding acid⁽⁴⁶⁾ and reduce this by the method of Goldberger⁽⁴⁷⁾. The hydrolysis proceeded satisfactorily but the reduction was not successful.

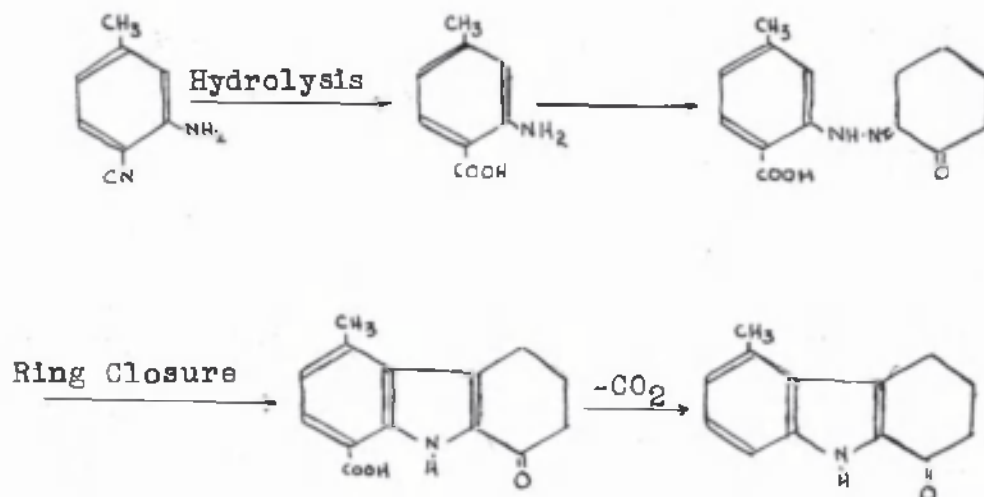
The most satisfactory method for the reduction of (II) was found to be that described by Bogert and Hoffman⁽⁴⁸⁾. The nitro-tolunitrile was added gradually to an excess of stannous chloride dissolved in concentrated hydrochloric acid, the temperature being maintained at 50-55°. The solution after reduction was diluted with alcohol and solid caustic potash added until almost neutral. The solution was then made slightly alkaline with ammonia and diluted with a large volume of alcohol. The precipitated tin hydroxide was filtered off and washed several times with alcohol. The combined alcoholic filtrates and washings were evaporated to small bulk, and poured into a large volume of water, when the 3-amino-4-cyano-toluene separated as a light brown crystalline powder, m.p. 93°, in 90% yield.

Cyclohexane-1:2-dione-1-(6¹-cyano-m-tolyl-hydrazone), (IV), was prepared by diazotising (III) and coupling with hydroxymethylene cyclohexanone prepared by the method already described (p.21).

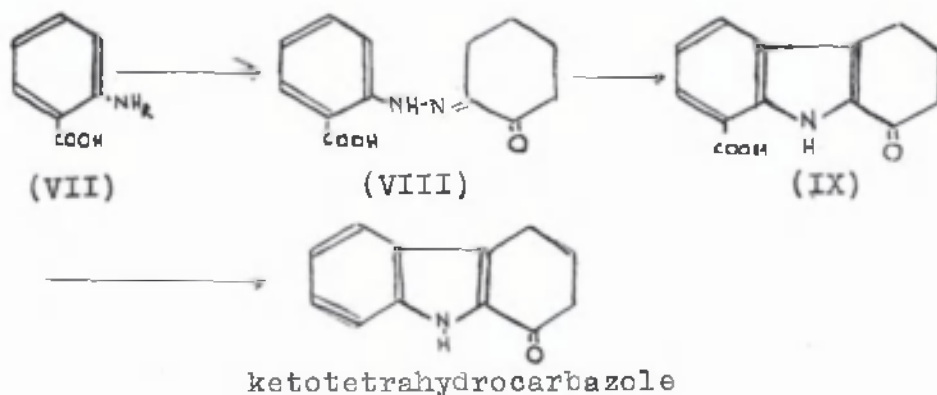
3-Amino-4-cyanotoluene (12 g.), finely-powdered, was suspended in concentrated hydrochloric acid (30 c.c.) diluted with water (30 c.c.) and sodium nitrite (7 g.) in a little water added slowly with stirring. A considerable amount of the diazo-amino compound was formed during the diazotisation (cf. 49, 50). The filtered diazo solution, after neutralisation, was added to a neutralised, diluted solution of hydroxymethylene cyclohexanone prepared from cyclohexanone (25 g.), ethyl formate (28 g.) and atomised sodium (7 g.) in the usual manner. A yellow oil was formed which on continued stirring turned red in colour and eventually solidified. This solid (8 g.) was recrystallised from alcohol and obtained as lustrous red crystals, m.p. 123° . (Found: N, 17.6. $C_{14}H_{15}ON_3$ requires 17.43%). The p-nitrophenylhydrazone was obtained from alcohol as small red-brown crystals, m.p. $214-215^{\circ}$. (Found: N, 22.4. $C_{20}H_{20}O_2N_6$ requires N, 22.3%)

Attempts to indolise this substance to 1-keto-5-methyl-8-cyano-tetrahydrocarbazole (V) by the method previously described (p.27) or by the use of dilute $H_2SO_4^{(51)}$, were completely unsuccessful.

The fact that ring closure was not obtained here led to a modification of the original scheme of synthesis. It was decided to attempt the synthesis in this fashion:-



To obtain information about the various reactions involved, a similar series of reactions was attempted, starting from anthranilic acid (VII) thus:-



The success of this series would be shown by the ultimate production of ketotetrahydrocarbazole, of which a sample was available for comparison purposes.

Cyclohexan-1:2-dione-mono-o-carboxyphenyl hydrazone (VIII) was prepared thus:-

Anthranilic acid (12 g.) was dissolved by boiling in hydrochloric acid (25 c.c. concentrated HCl and 25 c.c. water) and a fine suspension of the hydrochloride obtained by cooling and stirring. Water (10 c.c.) was added, and sodium nitrite (7 g. in 30 c.c. water) was slowly added with cooling and stirring. A clear red solution was obtained to which, after neutralising by the addition of excess sodium acetate and diluting with ice water (300 c.c.), a neutralised diluted solution of hydroxy methylene cyclohexanone, prepared from cyclohexanone (13.4 g.); ethyl formate (15 g.) and atomised sodium (5 g.), was added. The yellow oil which was precipitated solidified on stirring for some time and was filtered off and recrystallised from alcohol, when it was obtained as light brown prisms, m.p. 185-186°. (Found: N, 11.5. $C_{13}H_{14}O_3N_2$ requires 11.4%). The molecular weight, estimated by titration against standard alkali using phenolphthalein as indicator, was given as 246.9 against 246 required for $C_{13}H_{14}O_3N_2$.

1-Ketotetrahydrocarbazole-8-carboxylic acid (IX) was obtained in 80% yield by indolising (VIII) by the method previously described (p.27). It crystallised from alcohol as colourless needles, m.p. 279-281° (with sintering and darkening at 262°). (Found: N, 6.2. $C_{13}H_{11}O_3N$ requires N, 6.1%; molecular weight determined by titration against standard alkali, 229. $C_{13}H_{11}O_3N$ requires 229). An identical product is obtained by indolising (VIII) with 20% H_2SO_4 ⁽⁵¹⁾. The p-nitrobenzyl ester was obtained from alcohol as small colourless needles, m.p. 189°. (Found: N, 7.8. $C_{20}H_{16}O_5N_2$ requires N, 7.7%), and from this material the original acid was regenerated by boiling for 30 minutes with 10% alcoholic potash.

This acid was sparingly soluble in either hot or cold water; it dissolved slowly in cold alkali solutions, readily in hot, and a solution in hot moderately concentrated caustic soda yielded on cooling the sodium salt as colourless needles which did not melt below 300°. This salt on acidification yielded the original acid.

Attempted decarboxylation of 1-keto-8-carboxyketotetrahydrocarbazole.

Boiling with pure dry quinoline for 1 hour, or heating in a sealed tube with quinoline to 310° for five hours did not affect this acid.

Preliminary experiments showed that ketotetrahydrocarbazole sublimed unchanged under ordinary pressure at 240-280°. It was found however that the 8-carboxy compound also sublimed unchanged from 275-295°. Heating above 300° as described below evidently involved decomposition.

0.4 g. of the carboxy-ketotetrahydrocarbazole was placed in a narrow test tube attached to a thermometer, the whole being heated in an oil-bath. The test tube was fitted with a delivery tube dipping into lime water solution. At 280° the acid melted, on heating above 295° effervescence occurred, CO₂ being evolved. After the evolution of gas had ceased the tube was allowed to cool, and the black solidified contents extracted with boiling sodium carbonate solution and the residue extracted with alcohol. On diluting the alcoholic extract with water, a colloidal precipitate was obtained, m.p. 155-190°, which could not be obtained crystalline.

When the acid was heated above 300° in a sublimation apparatus a light yellow solid sublimed. This sublimate after extraction with hot sodium carbonate solution recrystallised from alcohol as colourless plates, m.p. 225-235°, mixed m.p. with the original acid 190-212°. It had a peculiar and unpleasant smell which persisted

after recrystallisation. A similar material was obtained by subliming in the presence of copper powder and by heating the acid or its sodium salt with soda-lime above 300° .

These results indicated that the heating of 1-keto-8-carboxy-tetrahydrocarbazole above the temperature at which it sublimed unchanged caused decomposition, with the production of an evil smelling substance which crystallised from alcohol as colourless plates, m.p. ca. $230-236^{\circ}$. No evidence of loss of water on heating was obtained; in fact the acid was returned unchanged on boiling for four hours with acetic anhydride.

The failure to remove the carboxyl group suggested that the corresponding 1-keto-5-methyl-8-carboxy-ketotetrahydrocarbazole if obtained would not lose carbon dioxide to give the desired 1-keto-5-methyl-tetrahydrocarbazole, and the synthesis of this substance was therefore abandoned.

Section C. The Preparation of Dibenzyltoluidines.

Desai⁽⁵²⁾, by heating equimolecular proportions of aniline and benzyl chloride for 6 hours at 97°C., obtained dibenzyl-aniline in 11% yield. The addition of 1% iodine increased the yield to 47%, while by adding 1% iodine and 90% sodium acetate (both calculated on the weight of aniline) a 98% yield was obtained.

By theory two molecular proportions of benzyl chloride are required for one of aniline. The preparation of dibenzyl-aniline using theoretical proportions of benzyl chloride and aniline, with the addition of double the amounts of iodine and sodium acetate recommended by Desai, was therefore investigated and the yield obtained compared with that from a similar preparation using Desai's quantities. This latter preparation gave a 90% yield (7.2 g. dibenzylaniline from 5 g. aniline and 6.3 g. benzylchloride) and that using the proportions theoretically demanded resulted in a yield of 81% (11 g. from 5 g. aniline and 12.6 g. benzyl chloride).

In both cases the product was a thick oil which was contaminated by unchanged starting materials. In one preparation using Desai's quantities the crude product was allowed to stand overnight with concentrated hydrochloric acid to remove the impurities. Such

treatment, however, was found to alter the crude material to a greenish-coloured solid, m.p. (ca.) 150-170°. It was further found that if pure dibenzyl-aniline were left in contact with cold concentrated hydrochloric acid for a day or two, it was transformed to a similar solid. This comparatively high melting material was not further investigated.

The following method for preparing the three isomeric dibenzyl-toluidines, based on the results obtained from these preliminary experiments, was found to give very good results.

6 c.c. of the appropriate toluidine, and 12.6 g. benzyl chloride, with the addition of 0.05 g. iodine, and 10 g. sodium acetate were heated under reflux for 6 hours at 100° in a brine bath. The reaction mixture was then treated with an excess of dilute hydrochloric acid and steam distilled until a clear distillate was given. The residue from steam distillation consisted of a heavy oil and a translucent supernatant liquor. The latter was decanted off and the oil (which was the crude dibenzyltoluidine) refrigerated until solid and recrystallised.

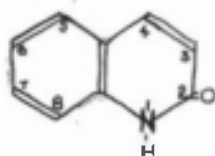
Dibenzyl-o-toluidine was obtained in 77% yield and crystallised from methyl alcohol as colourless prisms, m.p. 42°.

Dibenzyl-m-toluidine was obtained in 86% yield and crystallised from ethyl alcohol as colourless plates, m.p. 76-77°.

Dibenzyl-p-toluidine was obtained in 79% yield and crystallised from alcohol as colourless prisms, m.p. 55-56°.

The melting points are in agreement with those reported for the dibenzyl-toluidines by Courtot and Petitcolas⁽⁵³⁾.

Section D. Preparation of Methyl Derivatives of
Carbostyrl (I).



(I)

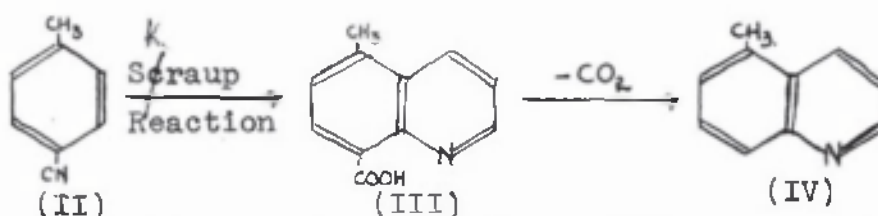
The six possible C-methyl derivatives of (I) were synthesised. Certain results obtained on investigating the behaviour of these derivatives towards poly-nitro substances (*vide infra*) made an investigation of the molecular compounds of 1-methylcarbostyrl interesting, and this substance was accordingly prepared. Also, advantage was taken of the accessibility of the 4:6-, 4:7, and 4:8-dimethyl derivatives to prepare these compounds and examine their molecular derivatives. With the exception of 4-methylcarbostyrl and the dimethyl derivatives mentioned, these methylcarbostyrils were all prepared from the corresponding quinolines.

1. Preparation of Methyl-Quinolines.

3-Methyl-quinoline was prepared by heating equimolecular quantities of freshly distilled propionaldehyde and o-aminobenzaldehyde for one hour at 220° (54)

The o-aminobenzaldehyde was obtained by reducing o-nitro-benzaldehyde by the method of Bamberger and Demuth⁽⁵⁵⁾.

5-Methyl-Quinoline was synthesised by the method of Jakubowski⁽⁵⁶⁾, which may be represented thus:-
or Jakubowski⁽⁵⁶⁾, which may be represented thus:-



3-Amino-4-cyano-toluene (II) was prepared from p-toluidine by the method already described (p.34).

5-Methyl-8-carboxy-quinoline (III) was obtained by subjecting (II) to a Skraup reaction, the cyano group being hydrolysed in the course of the reaction. Although the method for converting (II) to (III) given by Jakubowski was attempted several times, satisfactory results were not obtained. However, the following method, based on that described by Chakravarti and Venkatasubban⁽⁵⁷⁾, was found to give a reasonably good yield.

40 g. glycerol (previously dehydrated by heating to 180° for 30 minutes) with 20 g. arsenic oxide and 60 g. sulphuric acid (Sp.Gr. 1.84) were placed in a litre flask equipped with a reflux condenser and cautiously heated under a small flame. The contents of the flask gradually turned dark brown in colour, and a vigorous reaction was heralded by the appearance of bubbles on the surface. When this reaction commenced the amino-tolunitrile (20 g.) was added gradually, 2-3 g. at a time.

After all the aminotolunitrile had been added, the contents of the flask were heated in an oil bath at 145-155° for 7 hours, after which they were diluted with a litre of boiling water, and filtered to remove carbonised material. The filtrate was allowed to cool, made slightly alkaline with concentrated ammonia solution and, after being steam distilled to remove any 5-methyl quinoline formed during the reaction, was evaporated to small bulk, when a dirty brown crystalline solid (22 g.) was obtained. This was washed several times with water and extracted with alcohol. The alcoholic extract was purified with animal charcoal and evaporated to small bulk. On cooling the 5-methyl-8-carboxy quinoline crystallised out as small needles (18 g.). It was recrystallised from alcohol and obtained as colourless needles, m.p. 172-173°. This substance is identical with the 5-methyl-8-carboxy quinoline described by Jakubowski⁽⁵⁶⁾, yielding a picrate of similar melting point, and an insoluble nitrate which melts with decomposition at 215°.

The quantity of arsenic oxide used can be varied within limits. Preparations using 15, 20 and 25 g. of arsenic oxide for 20 g. aminotolunitrile all gave similar yields.

The decarboxylation of this acid was carried out by distilling the calcium salt⁽⁵⁶⁾, 60 g. of which

yielded on distillation 15 g. of an orange oil which on fractional distillation gave 9 g. 5-methyl quinoline (IV) as a yellow oil, b.p. 252-256°/758 m.m.

6-Methyl-quinoline, 7-methyl-quinoline, and 8-methyl-quinoline were prepared by Skraup syntheses from the corresponding toluidine⁽⁵⁸⁾.

2. Conversion of Methyl-Quinolines to Methyl-Carbostryls.

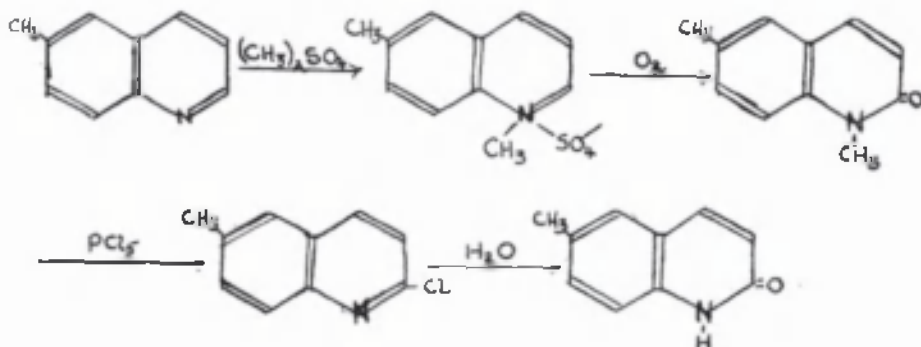
While the treatment of quinoline with bleaching powder gave carbostryl^{(59), (60)}, the 6- or 8-methyl derivatives could not be prepared in this way. It may be mentioned that Späth⁽⁶¹⁾, by treating 6:8-dimethyl quinoline with bleaching powder, did not obtain 6:8-dimethyl carbostryl; the chlorine according to Späth probably substituted in one of the methyl groups.

The next method attempted was that of Tschibabin⁽⁶²⁾ and his co-workers⁽⁶³⁾. These workers claim that by fusing quinoline (or a methylquinoline), dried over barium oxide, with powdered dry potassium hydroxide a good yield of carbostryl (or the appropriate methyl derivative) is obtained. Many attempts to repeat this work were made without success. According to Tschibabin the success of this method depends on (a) the

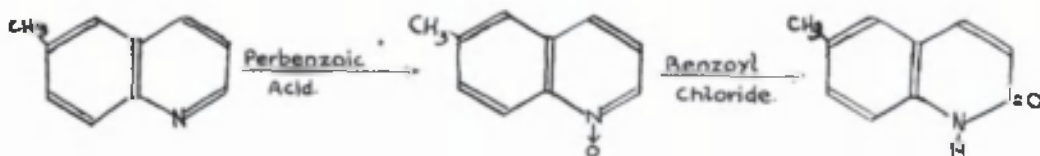
absolute dryness of the quinoline and potassium hydroxide, and (b) the fineness of division of the alkali. In our experiments every possible precaution against the introduction of moisture was taken. The quinoline was first distilled, allowed to stand in contact with fresh barium oxide for a considerable time, and finally distilled over barium oxide into the hot dry flask already containing the powdered KOH protected from atmospheric moisture by a calcium chloride tube. The caustic potash was first of all fused, maintained at a high temperature for some time, and the hot molten mass poured into a hot porcelain mortar, and allowed to cool in a desiccator until solid. It was then ground up as finely as possible before it was cool enough to be contaminated by atmospheric moisture and transferred to the dry flask into which the quinoline was later distilled; in some attempts the alkali was ground as finely as possible in a short time, in others it was ground up very finely, no account being taken of the time involved.

The first of the two successful methods used was that due to Späth⁽⁶¹⁾. This consisted in converting the methyl-quinoline to the corresponding methyl-quinolonium sulphate by the action of dimethyl sulphate, oxidising

this with potassium ferricyanide in alkaline solution to the corresponding N-methyl-carbostyryl, which on treatment with PCl_5 yielded the 2-chloro-derivative of the methyl quinoline used. By heating the chloro compound with water under pressure the required carbostyryl was obtained.



The second successful method was particularly valuable in those cases where only a small amount of the quinoline was available. This method was based on the method of converting quinoline to carbostyryl described by Henze⁽⁶⁴⁾. The methyl quinoline by the action of perbenzoic acid was converted to the methyl quinoline oxide which was isolated as its hydrochloride. The quinoline oxide hydrochloride when treated with benzoyl chloride in alkaline solution was converted to the desired methyl-carbostyryl.



The following detailed description of the preparation of 6-methyl-carbostyrl by each method will show the typical experimental procedure involved.

(a) By Späth's Method.

To 6-methyl-quinoline (10 g.) dissolved in dry benzene (50 g.) freshly distilled dimethyl sulphate (10 g.) was gradually added with shaking. The solution heated up and after a short time deposited crystals of the methyl quinolonium sulphate. After several hours these were dissolved by the addition of water (50 c.c.), and the resultant solution separated from the benzene and added gradually with cooling and stirring to a solution of potassium ferricyanide (47 g. in 100 c.c. water) to which had been added a solution of caustic potash (30 g. in 60 c.c. water). The reaction mixture was allowed to stand for three or four hours and then extracted three times with ether. On distilling off the ether the 1-6-dimethyl-carbostyrl was left behind as an oil which was distilled in vacuo when it was obtained as a colourless crystalline solid, m.p. 82-83°, b.p. 203-205°/15 m.m. Yield 7 g. Its picrate was obtained from alcohol as canary yellow needles, m.p. 150°. (Found: N, 13.8. $C_{11}H_{11}ON:C_6H_2(NO_2)_3.OH$ requires 13.9%*).

* Denotes microanalysis.

1:6-dimethyl-carbostyryl (5 g.) was heated with PCl_5 (7 g.) for half an hour at $135-140^\circ$. After cautious addition of ice-water to decompose excess PCl_5 the reaction mixture was steam distilled, when 2-chloro-6-methyl-quinoline (3 g.) was obtained as a colourless solid, which crystallised from alcohol as colourless plates, m.p. $114-115^\circ$. The yields obtained in this chlorination were found to vary considerably. The best yield was obtained by adding the minimum quantity of ice-water to decompose the excess PCl_5 gradually with external cooling. Chlorination by the use of PCl_5 in p-dichlorobenzene as solvent⁽⁶⁵⁾ was tried but did not give a good result.

2-Chloro-6-methyl-quinoline (1.5 g.) was converted to 6-methyl-carbostyryl (1.2 g.) by heating with water (30 c.c.) in a sealed tube for four hours at 190° . The 6-methyl-carbostyryl crystallised from alcohol as faintly yellow prisms, m.p. $233-234^\circ$. Its picrate crystallised from alcohol as pale yellow felted needles, m.p. $171-172^\circ$. (Found: N, 14.5%. $\text{C}_{10}\text{H}_9\text{ON}:\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}$ requires 14.4%).

(b). By Oxide Method.

A chloroform solution of perbenzoic acid was prepared thus⁽⁶⁶⁾:-

85 g. sodium peroxide were gradually added with stirring to 250 g. cracked ice in 400 c.c. water contained in a two litre beaker surrounded by a freezing mixture. When the temperature had fallen to 0° , benzoyl chloride (100 g.) was added gradually with vigorous stirring. When the addition was completed, the contents of the beaker were stirred for 6 hours, the temperature being maintained at $0 - 5^{\circ}\text{C}$. At intervals the lumps of dibenzoyl peroxide which formed were crushed. The contents of the beaker were filtered through a chilled Buchner funnel and the residual lumps of dibenzoyl peroxide crushed and stirred up with 600 c.c. ice-water, filtered, and the filtrate combined with the previous filtrate. These combined filtrates were then added with stirring to ice cold 10% sulphuric acid (600 c.c.) and chloroform (250 c.c.) The white crystalline perbenzoic acid which precipitated was immediately taken up by the chloroform. The chloroform extract was separated and the aqueous portion rapidly extracted twice with more chloroform. The chloroform extracts were combined and quickly dried over anhydrous sodium sulphate. The amount of active oxygen in this solution was estimated by titration⁽⁶⁷⁾.

In the first few preparations of perbenzoic acid only insignificant traces of active oxygen were obtained. The failure of these experiments was traced to the use of

a bronze stirrer, which apparently catalysed the decomposition of the perbenzoic acid. The substitution of a glass stirrer gave satisfactory results.

250 c.c. of this perbenzoic acid solution (containing 1 g. active oxygen) were added to 5 g. 6-methylquinoline in a clean dry flask and the resultant yellow solution allowed to stand for 24 hours and then extracted several times with 10% hydrochloric acid. By evaporating the acid extracts to dryness under reduced pressure the 6-methyl-quinoline oxide hydrochloride was obtained as a pale yellow crystalline solid (2 g.), which was washed with acetone and recrystallised from alcohol as colourless needles, m.p. 172-173°. (Found: N, 9.1. $C_{10}H_9ON$ requires 8.9%). Its picrate was obtained from alcohol as pale yellow felted needles, m.p. 174-175°. (Found: N, 14.2*. $C_{10}H_9ON:C_6H_2(NO_2)_3.OH$ requires 14.4%).

1.1 g. 6-methyl-quinoline oxide hydrochloride were dissolved in 25 c.c. water. To this solution were added solid caustic soda (0.6 g.) and benzoyl chloride (1 g.) drop by drop, with vigorous shaking after each addition. The contents of the flask were filtered, and the crude 6-methyl-carbostyryl (0.7 g.) thus obtained crystallised from alcohol. It crystallised as faintly yellow prisms, m.p. 232-233°; mixed m.p. with the 6-methyl-carbostyryl obtained by the first method 231-233°.

1-Methyl-carbostyryl⁽⁶⁸⁾ was obtained from quinoline by treating with dimethyl sulphate, and oxidising the resultant methyl quinolonium sulphate as described in the first method. It crystallised from petroleum ether as colourless needles, m.p. 72°.

3-Methyl-carbostyryl was prepared by the second method, by means of the corresponding 3-methyl-quinoline oxide hydrochloride. It crystallised from alcohol as colourless needles, m.p. 233-234°. (Found: N, 8.7. $C_{10}H_9ON$ requires 8.9%). Ornstein⁽⁶⁹⁾ who prepared this substance by heating the silver salt of 2-hydroxy-3-methyl-quinoline-4-carboxylic acid, describes it as yellowish needles, m.p. 234-235°. It has not previously been prepared from 3-methyl quinoline.

3-Methyl-quinoline oxide hydrochloride was obtained from alcohol as colourless prisms, m.p. 192-194°. (Found: N, 9.0%). Its picrate crystallised from alcohol as greenish yellow prismatic needles, m.p. 143-154° (incongruent). (Found: N, 14.4%).

An attempt was made to synthesise 3-methyl carbostyryl from o-aminobenzaldehyde and propionic anhydride, by the same method by which Camps⁽⁷⁰⁾ obtained carbostyryl from o-aminobenzaldehyde and acetic anhydride. The product, however, was not the propionyl drv. of amino-benzaldehyde but a white solid, given on recrystallisation

from acetone as colourless crystals, m.p. 225-227°, and probably formed by condensation of two or three molecules of the aminobenzaldehyde. No evidence of propionylation was obtained on boiling o-amino-benzaldehyde in propionic anhydride for 30 minutes.

5-Methyl-carbostyryl, which has not previously been described, was prepared from 5-methyl quinoline through its oxide as described in method (b). It crystallised from alcohol as colourless plates, m.p. 222-223°. (Found: N, 9.1%). Its picrate was obtained from alcohol as bright yellow prisms, m.p. 156-157°. (Found: N, 14.3%). Because of the small quantity available, the 5-methyl quinoline oxide hydrochloride was not investigated prior to conversion to the carbostyryl.

7-Methyl-carbostyryl, which has not so far been described, was obtained by Späth's method. It crystallised from alcohol as colourless plates, m.p. 192-193°. (Found: N, 8.9%). Its picrate was obtained from alcohol as light yellow felted needles, m.p. 163°. (Found: N, 14.3%). The intermediate substances, which appear to be new, prepared in this synthesis were:-

1:7-dimethyl-carbostyryl, obtained from petroleum ether as long, faintly yellow needles, m.p. 107-108°. (Found: N, 8.15. $C_{11}H_{11}ON$ requires 8.1%).

2-Chloro-7-methyl-quinoline, which crystallised from alcohol as colourless plates, m.p. 81° . (Found: N, 8.0; Cl, 19.8. $C_{10}H_8NCl$ requires N, 7.9%; Cl, 20.0%).

8-Methyl-carbostyryl was prepared by Spath's method and crystallised from alcohol as colourless prisms, m.p. 219° . Its picrate was obtained from alcohol as light yellow needles, m.p. $128-129^{\circ}$. (Found: N, 14.5%).

1-8-Dimethyl-carbostyryl picrate was obtained from alcohol as canary yellow, prismatic needles, m.p. 134° . (Found: N, 13.95%).

3. Preparation of 4-methyl carbostyryl and 4:6-, 4:7- and 4:8-dimethyl carbostyryls.

These were all prepared as described by Evans and King⁽⁷¹⁾. Aniline or the appropriate toluidine and acetoacetic ester in equimolecular proportion were boiled for a minute and a half. On cooling the acetoacetanilide (or toluidide) crystallised out. This was heated with concentrated sulphuric acid on the water bath for quarter of an hour and the mixture poured into water, when the desired carbostyryl derivative was precipitated.

On several occasions it was found that the acetoacetanilide did not crystallise out on cooling, the solution merely becoming very viscid. If this syrup were treated directly with concentrated sulphuric acid

on the water bath and then poured into water, the 4-methyl carbostyryl separated in a slightly impure form and the yield obtained in this way was actually found to be better than that obtained when the crystalline acetoacetanilide was filtered off before treatment with sulphuric acid.

4-Methyl-carbostyryl crystallised from alcohol as colourless prisms, m.p. 222° . Its picrate was obtained from alcohol as light yellow needles, m.p. $164-165^{\circ}$. (Found: N, $14.5\%^{*}$).

4:6-Dimethyl-carbostyryl was obtained from alcohol as colourless prisms, m.p. 250° . Its picrate was obtained from the same solvent as light yellow needles, m.p. 188° . (Found: N, $13.8\%^{*}$).

$C_{11}H_{11}ON:C_6H_2(NO_2)_3.OH$ requires N, 13.9%).

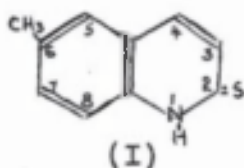
4:7-Dimethyl-carbostyryl crystallised from alcohol as colourless needles, m.p. 220° and its picrate was given from the same solvents as light yellow, felted needles, m.p. $189-191^{\circ}$. (Found: N, $13.9\%^{*}$).

4:8-Dimethyl-carbostyryl was obtained from alcohol as colourless, short, thick needles, m.p. $216-217^{\circ}$. Its picrate formed light canary yellow needles from alcohol, m.p. $192-194^{\circ}$. (Found: N, $13.7\%^{*}$).

Section B. Preparation of other Derivatives of
Carbostyryl.

The fact that the 6-methyl isomer was found to be unique among the methyl derivatives of carbostyryl in its indifference towards *s*-trinitrobenzene (p. 75), suggested the possibility that the 6-position might be directly concerned in the union of a methyl derivative of carbostyryl with a polynitro substance. To gain further information on this point and also to study the effect of replacing the oxygen of carbostyryl by sulphur, the following substances were prepared and their molecular derivatives investigated:-

6-Methyl-thiocarbostyryl (I) was prepared from 2-chloro-6-methyl quinoline as described by Fischer⁽⁷²⁾. It crystallised from alcohol as light yellow needles, m.p. 210°.



4-Methyl-thiocarbostyryl was prepared from 4-methyl-carbostyryl by the method described by Roos⁽⁶⁰⁾. It crystallised from alcohol as small greenish yellow needles, m.p. 265-267° (darkening at 240°).

4:6-Dimethyl-thiocarbostyryl, which had not previously been described, was obtained from 4:6-dimethyl-carbostyryl by a similar method thus:-

4:6-Dimethyl carbostyrl (3 g.) was finely powdered and intimately mixed with P_2S_5 (5 g.) and this mixture heated in a small flask, fitted with an air condenser and a calcium chloride tube, for two hours at 150° . Since at this temperature there was no obvious fusion, the temperature was raised to 210° and maintained there for one hour, at the end of which time the reaction mixture had the appearance of a dark brown glassy mass. The temperature was again lowered to 150° and kept there for a further three hours. The cold reaction product was a dark red glassy solid which was powdered and treated under reflux with 25 c.c. concentrated hydrochloric acid for about an hour. The hot acid solution was filtered through glass wool and diluted with cold water, when the 2-thio-4:6-dimethyl carbostyrl precipitated as a greenish yellow solid, which was recrystallised from alcohol and thus obtained as small sulphur-yellow needles, m.p. $295-298^\circ$ (darkening at 275°). (Found: N, 7.4%. $C_{11}H_{10}NS$ requires N, 7.4%).

1:6-Dimethyl-thiocarbostyrl, which is also apparently new, was obtained by a somewhat similar method, thus:-

1-6-Dimethyl-carbostyrl (3 g.) was heated with P_2S_5 (5 g.) for $4\frac{1}{2}$ hours at $130-135^\circ$. When the reaction product - a dark red glassy solid - had cooled, sodium hydroxide solution was added and the whole gently warmed

to decompose the excess P_2S_5 and, after the reaction had subsided, extracted with ether. Evaporation of the ether gave the 2-thio-1:6-dimethyl-carbostyrl as a yellow solid which crystallised from alcohol as small yellow needles, m.p. 137° . (Found: N, 7.5%*).

2-Methoxy-6-methyl quinoline (II) was prepared from 2-chloro-6-methyl quinoline as described by Späth⁽⁶¹⁾, and crystallised from alcohol as fine white needles, m.p. 63° . Its picrate formed greenish yellow plates from alcohol, m.p. $181-182^\circ$, with some previous softening. (Found: N, 13.9%*. $C_{11}H_{11}ON : C_6H_2(NO_2)_3.OH$ requires 13.9%).



(II)

Section E. The Preparation of Molecular Compounds.

1. General Method of Preparation.

The choice of solvent is an important factor in attempts to isolate crystalline molecular compounds. Bamberger and Dimroth⁽¹²⁾ show that, although two substances are capable of combining to form a binary additive compound, the possibility of isolating the crystalline compound from a solvent depends largely on the solubilities of the component substances. Where the solubilities are widely different no complex is obtained, and a complex isolated from a suitable solvent may be decomposed by attempted recrystallisation from a solvent in which the components exhibit widely different solubilities. The best solvent is therefore one in which both components dissolve fairly easily on heating and have a reasonably similar small solubility at the crystallisation temperature, i.e., room temperature. For the components used in this work, absolute alcohol possessed the properties desired. It will also be appreciated that comparison of stability, ease of formation, etc., can only be made if the same solvent is used throughout. In this work absolute alcohol was always the solvent tried first. Naturally in those cases where no complex was obtained from alcohol, other solvents, etc. were tried.

Unless otherwise stated, the molecular compounds described below were obtained by the following general method:-

About 0.1 g. of the "aromatic" component and an equimolecular amount of the "nitro" component were accurately weighed out into a clean dry test-tube and dissolved by boiling in absolute alcohol (usually 5-6 c.c.). The complex which crystallised out on cooling was filtered off and recrystallised from alcohol. The recrystallised specimen, after its homogeneity had been ascertained by microscopic examination, was combusted. The original filtrate was evaporated in stages and in this way "solution evidence" for the composition of the complex was obtained: where the composition was binary, homogeneous coloured complex was given to dryness, while from solutions which yielded ternary complexes the excess "nitro" substance was generally capable of isolation.

Where several analysis figures are given these derive from different specimens. Analyses marked with an asterisk were performed by micro methods.

2. Molecular Compounds of Derivatives of Keto-tetrahydrocarbazole (K).

(a) With *s*-trinitrobenzene.

2-Methyl-K. yielded two distinct additive

compounds. The first, of binary constitution formed light canary yellow needles, m.p. 180° . (Found: N, 13.7, 13.65%, 13.8. $C_6H_3(NO_2)_3 : C_{13}H_{13}ON$ requires 13.6%).

The second, of 1:2 composition, was obtained as golden yellow prismatic needles, m.p. $186-187^{\circ}$. (Found: N, 11.63, 11.48%, 11.50. $C_6H_3(NO_2)_3 : 2C_{13}H_{13}ON$ requires 11.45%).

This is the first recorded case in which complexes of alternative composition are given with s-T.N.B. Sudborough⁽¹⁵⁾ has described the isolation of 1:1 and 2:1 picrates of phenyl- β -naphthylamine, but no other case in which 1:1 and 1:2 derivatives are formed from the same components is known.

The binary complex was obtained from a solution containing the components in equimolecular proportion in a relatively large bulk of alcohol (0.1 g. s-T.N.B. : .093 g. 2-methyl-K. in 12 c.c. alcohol). It recrystallised unchanged from alcohol, but by crystallising from benzene was converted to the deeper coloured ternary modification. From the benzene filtrate from such a conversion excess s-T.N.B. was isolated.

The ternary complex was obtained from a benzene solution containing the components in either 1:1 or 1:2 proportions: in the former case excess T.N.B. was easily isolated by evaporating the filtrate. An alcoholic

solution containing the components in 1:2 proportions (.05 g. T.N.B.: .093 g. 2-methyl-K in 10 c.c. alcohol) deposited on cooling a mixture of both forms which on standing was gradually transformed into homogeneous ternary complex. This ternary compound recrystallised unchanged from benzene. Attempted recrystallisation from alcohol, however, led to the production of a mixture of the 1:1 and 1:2 forms, which mixture on standing in contact with the solution reverted to homogeneous 1:2 complex.

3-Methyl-K yielded a 1:2 complex as deep golden yellow needles, m.p. 187-188°. (Found: N, 11.52%).

"Solution evidence" was obtained for 1:2 composition.

4-Methyl-K yielded a 1:2 complex as deep golden yellow needles, m.p. 177°. (Found: N, 11.56%). The "solution evidence" corroborated the ternary constitution shown by analysis.

5 (or 7)-Methyl-K gave a 1:2 derivative as orange-yellow felted needles, m.p. 190-192°. (Found: n, 11.5*%).

6-Methyl-K gave a 1:1 complex as yellow fluffy needles which recrystallised unchanged from benzene, m.p. 174-176°. (Found: N, 13.5*%). No excess s-T.N.B. was isolated from a solution containing the components in 1:1 proportion.

7 (or 5)-Methyl-K yielded a 1:2 derivative as

orange-yellow fine needles, m.p. 201-203°. (Found: N, 11.7%). "Solution evidence" was obtained for 1:2 composition.

8-Methyl-K. yielded a 1:1 complex as golden yellow felted needles, m.p. 179-180°. (Found: N, 13.7*, 13.7%). The binary composition of this complex was supported by "solution evidence".

5:6-Benzo-K. gave a 1:1 derivative from acetic acid as yellow fibrous needles, m.p. 229-231°. (Found: N, 12.7. $C_6H_3(NO_3)_3 : C_{16}H_{13}ON$ requires N, 12.5%).

7:8-Benzo-K. gave a 1:1 derivative from acetic acid as bright yellow needles, m.p. 240-241°. (Found: N, 12.3%).

The complexes of the benzoketotetrahydro-carbazoles could be prepared from alcohol but were very insoluble in this solvent and required a considerable volume for solution. They were reasonably soluble in acetic acid which was found to be the most convenient solvent to use.

(b) With Picric Acid.

2-Methyl-K. gave a 1:2 complex as orange-red felted needles, m.p. 154-155° with slight previous sintering. (Found: N, 11.31, 11.27, 11.20*, 11.22. $C_6H_2(NO_2)_3.OH : 2C_{13}H_{13}ON$ requires 11.2%). Excess picric

acid was isolated from a solution containing the components in equimolecular proportion. No evidence of an alternative binary complex was obtained.

3-Methyl-K. yielded a 1:2 picrate from benzene as orange red flat needles, m.p. 169° with some previous softening. (Found: N, 11.48%). "Solution evidence" was obtained for 1:2 composition. This complex was dissociated into its components by attempted crystallisation from alcohol.

4-Methyl-K. gave a 1:2 derivative as red needles, m.p. $157-159^{\circ}$ with previous sintering. (Found: N, 11.2%). The "solution evidence" was in agreement with 1:2 composition.

5 (or 7)-Methyl-K. gave a 1:2 picrate as red fine needles, m.p. $158-159^{\circ}$. (Found: N, 11.18*%).

6-Methyl-K. yielded a 1:1 derivative as small, buff coloured needles, m.p. $156-158^{\circ}$. (Found: N, 13.1%. $C_6H_2(NO_2)_3OH:C_{13}H_{13}ON$ requires 13.1%). This picrate recrystallised unchanged from benzene and the "solution evidence" agreed with 1:1 composition.

7 (or 5)-Methyl-K. yielded a 1:2 derivative as orange red needles or plates, m.p. 183° . (Found: N, 11.1%, 11.2%). This complex recrystallised unchanged from benzene. "Solution evidence" supporting 1:2 composition was obtained.

8-Methyl-K. yielded a 1:1 picrate as orange red needles, m.p. 161-162°. (Found: N, 13.2%).

5:6-Benzo-K. gave a 1:1 picrate from acetic acid as light red fibrous needles, m.p. 212-214° (with decomposition). (Found: N, 12.2. $C_6H_2(NO_3)_2.OH:C_{16}H_{13}ON$ requires 12.1%).

7:8-Benzo-K. gave a 1:1 picrate from acetic acid as red needles, m.p. 220-222° (with decomposition). (Found: N, 12.3%).

Like the corresponding s-T.N.B. derivatives the picrates of the benzoketotetrahydrocarbazoles could be formed in alcohol but were very sparingly soluble in that solvent even on heating.

(c) With m-dinitrobenzene.

6-Methyl-K. yielded an unstable 1:1 derivative as yellow needles, m.p. 125-150° (incongruent). (Found: N, 11.4%. $C_6H_4(NO_2)_2:C_{13}H_{13}ON$ requires 11.45%). This complex was partially decomposed into its colourless components on attempted recrystallisation from a relatively large bulk of alcohol.

8-Methyl-K. gave an unstable 1:2 complex as yellow plates, m.p. 106-138° (incongruent). (Found: N, 9.9%, 9.8%. $C_6H_4(NO_2)_2:2C_{13}H_{13}ON$ requires N, 9.9%).

This complex can be obtained from alcohol only when an excess of m-dinitrobenzene is present. It is decomposed by attempted recrystallisation from this solvent.

3. "Mixed" Molecular Compounds of 5 (or 7)-Methyl and 7 (or 5) Methyl-Ketotetrahydrocarbazoles.

So far three "mixed" molecular compounds, two picrates and one *s*-trinitrobenzene derivative have been isolated. In these both isomeric ketotetrahydrocarbazoles are in some way held in combination with the "nitro" substance so that they possess three distinct components, two "aromatic" components and one "nitro" component. These "mixed" derivatives isolated are:-

(A) A ternary picrate as deep red, well-formed prisms or prismatic needles, m.p. 153-154° with sintering at 135° and softening at 148°. (Found: N, 11.1; 11.0%; 11.2. 1:2 derivative requires N, 11.18%). The percentage of picric acid, estimated by washing out the picric acid from a weighed quantity of the complex by treatment with ammonia solution and weighing the residual material, was given as 37.2 and, for a different specimen, 37.4, against 36.7% required for 1:2 composition. The mixture of methyl ketotetrahydrocarbazoles left on removal of the picric acid melts (ca.) 134-150°. (Found: N, 7.17; 7.23. $C_{13}H_{13}ON$ requires 7.03%).

When the mixture of 5 (or 7)- and 7 (or 5)-methyl ketotetrahydrocarbazoles obtained by indolising cyclohexan-1:2-dione mono-m-tolylhydrazone was treated with half a molecular proportion of picric acid in alcohol (as described on p.31) the picrate of the 7 (or 5)-methyl isomer was first of all obtained. By reducing the volume of the filtrate in stages, the deep red "mixed" picrate was obtained (p. 31). It was also obtained from the mixture of isomers, m.p. 125-140°, which was left after separation of pure 7 (or 5)-methyl ketotetrahydrocarbazole by adding successive small quantities of boiling water to the indolisation mixture as described on p.30. By treating the mixture, depleted of the 7 (or 5)-methyl isomer in this way with half a molecular proportion of picric acid in alcohol the "mixed" ternary complex crystallised out. It recrystallised from a small amount of alcohol (.1 g. in 4 c.c.) but from a large amount of alcohol (.1 g. in 10 c.c.) it is partially converted to a light orange yellow modification (vide infra); attempted recrystallisation from a solution of picric acid in alcohol converted it completely into this lighter coloured complex.

(B). A binary picrate as light orange yellow prismatic needles, m.p. 145-151° with sintering at 135°

(Found: N, 13.3; 13.4*; Picric acid, 55.0. 1:1 composition requires N, 13.1% and picric acid, 53.5%). The material obtained by removing the picric acid melts ca. 155-163°; hence this binary substance contains the isomers in a proportion different from that in which they occur in the deeper-coloured ternary modification, apparently containing a relatively greater amount of the higher-melting 7 (or 5)-methyl isomer. This light orange yellow binary complex was obtained when attempts were made to recrystallise the red ternary "mixed" picrate from a relatively large amount of alcohol or from alcohol containing excess picric acid. It recrystallised unchanged from a large bulk of alcohol (.5 g. in 25 c.c.), or from a small quantity containing an excess of picric acid. Attempted recrystallisation from more concentrated alcoholic solution (.1 g. in 2.5 c.c.) resulted in a complete or (more usually) partial conversion to the deep red ternary form.

(C) A ternary s-trinitrobenzene derivative as light red glistening needles, m.p. 180°. (Found: N, 11.5. 1:2 composition requires N, 11.45%). This derivative was obtained when the mixture of isomers obtained by decomposing the deep-red ternary picrate with ammonia was treated with s-trinitrobenzene ($\frac{1}{2}$ molecule) in alcohol. By evaporating this solution in stages to dryness, the "mixed" s-trinitrobenzene derivative was obtained without

serious alteration to dryness; it appears therefore that the proportion of the "aromatic" isomers in this derivative is the same as that in which they occur in the deep red 1:2 picrate. It recrystallised from alcohol and no evidence has so far been obtained that it can be converted to a binary modification.

Owing to the inaccessibility of the 5 (or 7)-methyl-ketotetrahydrocarbazole (c.f., p. 31), it has not yet been possible to determine the proportions in which the isomeric methyl ketotetrahydrocarbazoles occur in these "mixed" molecular derivatives.

4. Molecular Compounds of the Dibenzyl-Toluidines and o-Trinitrobenzene.

Dibenzyl-o-toluidine did not yield a crystalline complex. A solution in alcohol containing the components in equimolecular proportion was light yellow in colour - much lighter in colour than corresponding solutions containing the m or p isomers - but no crystalline complex deposited on standing.

Thermal analysis was found to be useless in this case, since mixtures of the components fused to oils which in some cases did not solidify after standing for 48 hours at 0°C.

Dibenzyl-m-toluidine yielded a 2:3 complex from alcohol as ruby red prisms, m.p. 71-72°. (Found: N, 9.9; 9.8. $2.C_6H_3(NO_2)_3:3C_{21}H_{21}N$ requires 9.7%). The isolation of this substance gave some difficulty. A solution in alcohol containing the components in 1:2 proportion (0.3 g. d.b.-m-tol.: 0.1 g. T.N.B.) was deep red in colour: on standing a mixture of both components was deposited and the solution colour lightened considerably. 2 c.c. alcohol were added and the solid material was redissolved. No crystals were deposited on standing for 10 days, and any attempt to reduce the bulk of the solution resulted in the deposition of a mixture of both components. Solutions in benzene containing the components in 1:1 or 1:2 proportion behaved similarly.

The deep solution colours indicated that a complex was present and it was anticipated that this would probably be similar in composition to, and, considering the similarity in structure of the components, possibly isomorphous with the ternary complex of dibenzylaniline and *s*-trinitrobenzene. The 1:2 alcoholic solution which had stood for some time without depositing solid material was therefore "seeded" with a crushed crystal of the dibenzylaniline-trinitrobenzene complex. After a few

moments the solution deposited the complex described.

An alcoholic solution containing the components in 1:1 proportion (0.13 g. d.b.m-tol.: 0.1 g. T.N.B. in 5 c.c.) when "seeded" with either dibenzylaniline-trinitrobenzene complex or previously prepared dibenzyl m-toluidine-trinitrobenzene complex, deposited microscopically homogeneous complex. This substance was never obtained without "seeding". A solution of the components in 2:3 proportion in alcohol stood undisturbed for several weeks in a thermostat without depositing solid material; when this solution was seeded homogeneous complex was deposited after a short time.

This is the first recorded case of a trinitrobenzene derivative of 2:3 composition. Additional evidence for this composition was obtained when the melting points of mixtures of the components were investigated. Mixtures of 1:1 and 1:2 compositions began to melt at 56°, at 64° were half melted, and at 66-67° completely melted. These melts, which were deep red in colour, on cooling changed to colourless solids. A 2:3 mixture however melted at 67-69° and on cooling gave a mixture of red prisms and colourless material.

Dibenzyl-p-toluidine gave a 1:2 complex from alcohol, without "seeding", as deep ruby red needles, m.p. 62-64°. (Found: N, 8.9. $C_6H_3(NO_2)_3 \cdot 2C_{21}H_{21}ON$)

requires N, 8.9%).

5. Molecular Compounds of C-Methyl Derivatives of Carbostryl with s-Trinitrobenzene.

3-Methyl-Carbostryl yielded a 1:2 derivative as light yellow prismatic needles, m.p. 182-213° (incongruent). (Found: N, 13.08. $C_6H_3(NO_2)_3:2C_{10}H_9ON$ requires 13.18%).

This substance also gave a 1:2 molecular picrate as golden yellow prisms, m.p. 160-201° (incongruent) from alcohol. (Found: N, 12.6*, 12.5*.

$C_6H_2(NO_2)_3.OH:2C_{10}H_9ON$ requires N, 12.8%).

4-Methyl-carbostryl readily gave a 1:2 complex as canary yellow prisms, m.p. 226-227°. (Found: N, 13.05%) This complex is rather insoluble in alcohol. It is identical with the trinitrobenzene derivative of "hydroxy-lepidine" reported by Sudborough⁽⁸⁾.

5-Methyl-carbostryl gave a 1:2 derivative as light yellow prismatic needles, m.p. 222-223°. (Found: N, 13.1%).

6-Methyl-carbostryl did not yield a crystalline derivative with s-trinitrobenzene. Solutions containing the components in various proportions in alcohol, acetone, benzene, ether, petroleum ether, chloroform, etc. were investigated but no solid complex was obtained. Such

solutions were in general faintly yellow and much lighter in colour than the corresponding solutions containing the other isomeric methyl carbostyrils. A melting point curve of the components (given on p.82) shows no indication of a ternary complex.

7-Methyl-carbostyril gave a 1:2 complex as canary yellow needles, m.p. 203-204°. (Found: N, 13.3; 13.4%).

8-Methyl-carbostyril gave a 1:2 complex as golden yellow needles, m.p. 181°. (Found: N, 13.22%; 13.18%).

4:6-Dimethyl-carbostyril yielded a 1:2 derivative as bright golden yellow prisms, m.p. 198-217° (incongruent). (Found: N, 12.7%. $C_6H_3(NO_2)_3:2C_{11}H_{11}ON$ requires 12.5%). This complex could be formed and recrystallised only from a small amount of alcohol. Where the solution was too dilute (e.g., .1 g. complex in 7.5 c.c. alcohol), 4-6-dimethyl carbostyril deposited on cooling.

4:7-Dimethyl-carbostyril yielded a stable 1:2 complex as sulphur yellow needles, m.p. 213-214°. (Found: N, 12.3%).

4:8-Dimethyl-carbostyril yielded a stable 1:2 derivative as sulphur yellow small needles, m.p. 199-200°. (Found: N, 12.48%).

The composition of those complexes of 6-methyl derivatives of carbostyril was shown by "solution evidence" as well as by combustion.

6. Molecular Compounds of Certain other
Derivatives of Carbostyryl.

4-Methyl-thiocarbostyryl with s-trinitrobenzene gave a 1:2 complex as deep brownish yellow well-formed prisms, m.p. 190-192° (with previous softening) from an acetic acid solution containing excess trinitrobenzene. (Found: N, 12.4. $C_6H_3(NO_2)_3:2C_{10}H_9NS$ requires N, 12.3%). This complex could not be prepared from alcohol or benzene in which the "aromatic" component is very sparingly soluble, and it was decomposed by attempted recrystallisation from these solvents. It was not formed from acetic acid unless excess s-trinitrobenzene was present.

With Picric Acid. A molecular compound of 1:2 composition was obtained as orange red plates, m.p. 193-195° with some decomposition. (Found: N, 11.9. $C_6H_2(NO_2)_3.OH:2C_{10}H_9NS$ requires 12.1%). This complex was obtained from a chloroform solution of the components containing excess picric acid (.08 g. 4-me-thioC.: 0.15 g. P.A. in 5 c.c. alcohol). It could not be prepared from solutions of the components in alcohol, benzene, or acetic acid even when these contained excess picric acid, nor was it obtained from a chloroform solution which did not contain excess picric acid.

6-Methyl-thiocarbostyryl with s-trinitrobenzene gave a 1:2 molecular compound as orange prisms, m.p. 159-161°. (Found: N, 12.53%). This complex was somewhat unstable, and attempted recrystallisation from a relatively large bulk of alcohol resulted in the precipitation of the "aromatic" constituent.

With Picric Acid. A molecular complex of 1:1 composition was obtained as scarlet prisms, m.p. 140-142°. (Found: 13.7. $C_6H_2(NO_2)_3 \cdot OH : C_{10}H_9NS$ requires 13.86%). This complex could not be obtained from alcohol or benzene and was decomposed by attempted recrystallisation from these solvents. It was prepared from a chloroform solution containing the constituents in 1:1 proportion (.1 g. P.A.: .076 g. 6-me-2 thio-C. in 3 c.c. $CHCl_3$).

1:6-Dimethyl-thiocarbostyryl could not be made to give crystalline additive complexes with either s-trinitrobenzene or picric acid, although the solutions of components in various solvents were deep golden yellow in colour.

4:6-Dimethyl-thiocarbostyryl showed no evidence of complex formation with s-trinitrobenzene or picric acid. This may be due to its very slight solubility in the usual organic solvents.

2-Methoxy-6-methyl-guinoiline with s-trinitrobenzene gave a 1:1 complex as light greenish yellow

prisms, m.p. 72-73°. (Found: N, 14.5. $C_6H_3(NO_2)_3$: $C_{11}H_{11}ON$ requires 14.4%). This complex is comparatively unstable in alcohol and can only be prepared or recrystallised from small bulk.

No crystalline complexes were isolated from solutions of 1-methyl-carbostyryl, 1:6-dimethyl-carbostyryl, or 1:8-dimethyl-carbostyryl, and s-trinitrobenzene.

TABLE I.

"Aromatic" Component.	"Nitro" Component.	Complex			Page No.
		Comp	M.P.	Colour	
2-Methyl K.	T.N.B.	1:1	180°	light yellow	64
"	"	1:2	186-187°	golden yellow	"
"	P.A.	1:2	154-155°	orange yellow	66
3-Methyl K.	T.N.B.	1:2	187-188°	golden yellow	65
"	P.A.	1:2	169°	orange red	67
4-Methyl-K.	T.N.B.	1:2	177°	golden yellow	65
"	P.A.	1:2	157-159°	red	67
5(or 7)-Methyl K.	T.N.B.	1:2	190-192°	orange yellow	65
"	P.A.	1:2	158-159°	red	67
6-Methyl-K.	T.N.B.	1:1	174-176°	yellow	65
"	P.A.	1:1	156-158°	buff	67
"	m-D.N.B.	1:1	incong.	yellow	68
7(or 5)-Methyl K.	T.N.B.	1:2	201-203°	orange yellow	65
"	P.A.	1:2	183°	orange red	67
8-Methyl-K.	T.N.B.	1:1	179-180°	golden yellow	66
"	P.A.	1:1	161-162°	orange red	68
"	m-D.N.B.	1:2	incong.	yellow	68

PART 3. DISCUSSION.

I. Complexes of Monomethyl derivatives.

Of the seven monomethyl derivatives of ketotetrahydrocarbazole (K.) whose molecular derivatives with *s*-trinitrobenzene (T.N.B.), picric acid (P.A.) and *m*-dinitrobenzene (*m*-D.N.B.) are shown in Table I; six form derivatives of 1:2 composition; of the seventeen crystalline complexes isolated eleven, or about 65%, are ternary. Only in the case of 6-methyl K. is this property not demonstrated, although 8-methyl-K., like tetramethyldiaminodiphenylmethane⁽¹⁹⁾, displays its capacity to yield 1:2 complexes not towards T.N.B. or P.A., but towards *m*-D.N.B.

The crystalline complexes isolated from the dibenzyltoluidines are shown in Table II. The two crystalline derivatives obtained are both of irregular composition. That from dibenzyl-*m*-toluidine is the only case known of a crystalline 2:3 derivative; a complex of similar constitution is indicated on the melting-point curve of triphenyl carbinol and T.N.B.⁽⁷⁴⁾. This complex of dibenzyl-*m*-toluidine is peculiar in that it could only be obtained by "seeding" with either a crystal of previously prepared complex or (as it was obtained in the first instance) a crystal of the 1:2 complex of dibenzyl-

TABLE II.

"Aromatic" Component	"Nitro" Component.	Complex			Page No.
		Comp.	M. P.	Colour	
Dibenzyl- <u>o</u> -toluidine	T.N.B.	-	-	-	72
Dibenzyl- <u>m</u> -toluidine	"	2:3	71-72°	Ruby red	73
Dibenzyl- <u>p</u> -toluidine	"	1:2	62-64°	deep ruby red	74

TABLE III.

"Aromatic" Component	"Nitro" Component.	Complex			Page No.
		Comp.	M. P.	Colour	
3-Methyl-C.	T.N.B.	1:2	incong.	Light yellow	75
"	P.A.	1:2	"	bright yellow	75
4-Methyl-C.	T.N.B.	1:2	226-227°	canary yellow	75
5-Methyl-C.	"	1:2	222-223°	light yellow	75
6-Methyl-C.	"	1:1?	-	-	75
7-Methyl-C.	"	1:2	203-204°	canary yellow	76
8-Methyl-C.	"	1:2	181°	golden yellow	76

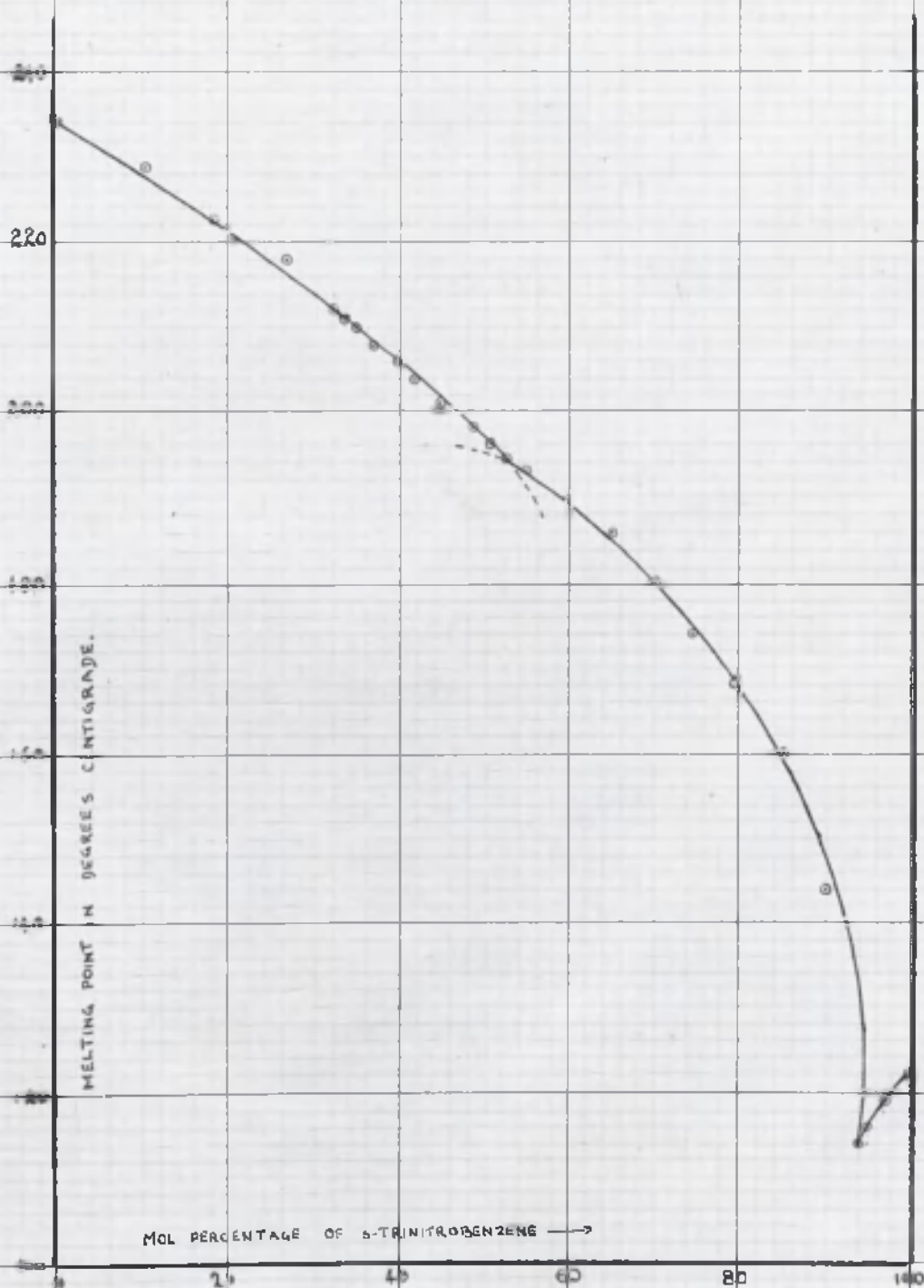
aniline and T.N.B. The suitability of the crystal-lattice therefore appears to be a factor in this case. Both 1:1 and 1:2 forms are apparently present in solution and by presenting a specimen of a suitable crystal-lattice (by "seeding") the two forms crystallise out together as a homogeneous 2:3 complex. Although solutions and melts of the components were coloured, no crystalline derivative of the ortho isomer and T.N.B. was isolated.

Of the molecular complexes formed by the monomethyl derivatives of carbostyryl (C.), which are shown in Table III, a high proportion, six out of seven or about 85%, are ternary in composition. 6-methyl-C., like the corresponding derivative in the ketotetrahydrocarbazole series, is unique in failing to demonstrate the capacity to form 1:2 derivatives. In this case no crystalline binary complex is formed, although the melting point curve (given on next page) indicates the formation of a very unstable binary complex.

With the exception of 3-methyl-C., the methyl derivatives of C. do not form true molecular picrates. Compared with the corresponding T.N.B. derivatives the picrates do not display the deepening in colour and consistent lowering of melting point which Pfeiffer⁽⁹⁾ has shown are characteristic of molecular picrates, and which are well illustrated by the molecular picrates of monomethyl

MELTING-POINT CURVE OF SYSTEM6-METHYL-CARBOSTYRIL ~ 5-TRINITROBENZENE

The relevant figures are tabulated overleaf



MELTING-POINTS OF MIXTURES OF
6-METHYL-CARBOSTYRIL AND 5-T.N.B.

WEIGHT OF 5-TRINITRO- BENZENE g.	WEIGHT OF 6-METHYL CARBOSTYRIL g.	% TRINITRO- BENZENE	TEMP. AT WHICH LAST TRACE OF SOLID DISAPPEARS. °C
—	—	0.0	234
·0246	·1582	10.55	229
·0259	·0757	18.37	222.5
·0272	·0562	26.5	218
·0247	·0389	32.15	212
·0243	·0362	33.4	211
·0251	·0347	35.05	210
·0253	·0318	37.3	208
·0254	·0288	39.7	206
·0244	·0254	41.8	204
·0267	·0246	44.8	201.5
·0313	·0250	48.3	198
·0342	·0250	50.5	196
·0375	·0249	52.4	194.5
·0410	·0252	54.8	193
·0499	·0250	59.8	189.5
·0624	·0251	65.0	186
·0780	·0247	70.21	180.5
·1010	·0254	74.82	176
·1349	·0258	79.6	168.5
·1896	·0241	85.5	160
·3026	·0253	89.95	144
·5244	·0250	94.0	114
·6374	·0247	95.06	116
1.0815	·0248	97.05	119
—	—	100.0	122

derivatives of K. (Table I). The fact that they differ in composition from the corresponding T.N.B. derivatives and the formation of a stable picrate by 6-methyl-C., which does not yield a crystalline T.N.B. dvt., is further evidence that these picrates are salt-like in character (comparable to either the ammonia and aniline type of picrates or to coumarin picrate⁽⁷⁵⁾). The picrates of the N-methyl and O-methyl derivatives of C. are similar. The substitution of sulphur for oxygen in carbostyryl derivatives, however, confers the property of forming deeply coloured molecular picrates (see Nos.9-13 in Table IV). On the basis of Hertel's work⁽²⁹⁾, therefore, methylation in the 3-position or the substitution of sulphur for oxygen in carbostyryl evidently causes a reduction in basicity sufficient to alter the nature of the picrates formed.

The significance of these results from the monomethyl derivatives of ketotetrahydrocarbazole, dibenzyl-aniline and carbostyryl is at once apparent. In a systematic examination of three different series in which any constitutional factor conditioning the formation of 1:2 derivatives is maintained more or less at an optimum while other factors, not directly related to component constitution fluctuate normally, the proportion of ternary derivatives was found to be 65%, 66% and 85%. These

TABLE IV.

No.	"Aromatic" Component	"Nitro" Component.	Complex			Page No.
			Comp	M.P.	Colour	
1	4:6-Dimethyl-C.	T.N.B.	1:2	incong.	bright yellow	76
2	4:7-Dimethyl-C.	"	1:2	213-214°	pale yellow	76
3	4:8-Dimethyl-C.	"	1:2	199-200°	pale yellow	76
4	C.-Methyl ether	"	1:1	90°	light brown	Ref. 73
5	6-Methyl-C- methyl ether	"	1:1	72-73°	yellow	78
6	1-Methyl-C.	"	-	-	-	79
7	1:6-Dimethyl-C.	"	-	-	-	79
8	1:8-Dimethyl-C.	"	-	-	-	79
9	Thio-C.	"	1:1	165°	light brown	Ref. 73
	"	P.A.	1:1	145°	crimson	"
10	4-Methyl-Thio-C.	T.N.B.	1:2	190-192°	light brown	77
	"	P.A.	1:2	193-195°	orange red	77
11	6-Methyl-Thio-C.	T.N.B.	1:2	159-161°	orange	78
	"	P.A.	1:1	140-142°	scarlet	78
12	1-Methyl-Thio-C.	T.N.B.	1:2	99°	orange	Ref. 73
	"	P.A.	1:2	104°	"	"
13	1:6-Dimethyl- Thio-C.	T.N.B.	-	-	solutions are	78
	"	P.A.	-	-	coloured	78
14	4:6-Dimethyl- Thio-C.	T.N.B.	-	-	-	78
	"	P.A.	-	-	-	78

figures, contrasted with the usual 1-2% incidence of such abnormal complexes found by Pfeiffer in his general survey, prove conclusively that the primary factor conditioning the formation of ternary molecular compounds of aromatic polynitro substances is constitutional. Complexes of 1:2 composition are therefore characteristic of certain aromatic components which possess some particular property inherent in their chemical structure.

This point could not have been conclusively established had the investigation not been systematic; the results obtained justify the preparation and investigation of the more inaccessible "aromatic" components. If the investigation had been confined to the easily prepared 6- and 8-methyl derivatives of ketotetrahydrocarbazole and carbostyryl no useful conclusions could have been drawn from the results obtained.

2. Complexes of Other Derivatives.

The complexes formed by the other "aromatic" substances prepared are given in Table IV. It will be seen that the capacity to yield ternary derivatives may survive dimethylation (Nos.1-3) or substitution of sulphur for oxygen (Nos.9-12), and is not therefore so transient as previously recorded instances might suggest (see p.11).

TABLE V.

"Aromatic" Component	"Nitro" Component	Complex			Page
		Comp	M. P.	Stability	No.
Carbostyrl (C)	T.N.B.	1:2	178°	Stable in alcohol	Ref.15
6-Methyl-C	"	1:1?	-	very unstable	75
4-Methyl-C	"	1:2	226-227°	stable in alcohol	75
4:6-Dimethyl-C	"	1:2	incong.	unstable in dilute alcohol	76
Thio-C.	T.N.B.	1:1	165°	stable in alcohol	Ref.73
"	P.A.	1:1	145°	" "	"
6-Methyl-Thio-C.	T.N.B.	1:2	159-161°	unstable in large amount of alcohol	78
"	P.A.	1:1	140-142°	unstable in alcohol	"
1-Methyl-Thio-C.	T.N.B.	1:2	99°	stable in alcohol	Ref.73
"	P.A.	1:2	104°	" "	"
1:6-Dimethyl-Thio-C.	T.N.B.	-	-	no crystalline	78
"	P.A.	-	-	dvts. obtained	"
C-O-Methyl ether	T.N.B.	1:1	90°	stable in alcohol	Ref.73
6-Methyl-C-O methyl ether	T.N.B.	1:1	72-73°	unstable in large bulk of alcohol	78

Methylation of the oxygen in carbostyryl (Nos. 4 and 5) however apparently leads to a disappearance of the capacity to give 1:2 derivatives.

Methylation of the nitrogen in carbostyryl and its derivatives (Nos. 6-8) evidently causes a considerable reduction in combining capacity, for none of the N-methylated derivatives investigated gave crystalline derivatives.

6-Methyl carbostyryl is unique among the members of its series (Table III) in its total failure to yield crystalline molecular derivatives, a fact which seemed to suggest that this position might be actively engaged in the union of the components in the formation of molecular complexes of these substances. This, coupled with the fact that methylation in the corresponding position in ketotetrahydrocarbazole has the most pronounced effect on complex constitution (6-methyl-K and the benzo-Ks, [pp. 66, 68] which are also substituted in the 6-position, are the derivatives of K. examined which fail to display the capacity to yield 1:2 derivatives), suggested that further investigation of the effect of methylation in the 6-position in derivatives of carbostyryl might furnish interesting results. The results obtained are summarised in Table V in which the complexes furnished by 6-methylated derivatives of carbostyryl (C.) are compared with the corresponding complexes given by the unmethylated substances.

It will be seen from the table that although in some cases methylation in this position causes a change in the composition of the complex formed, it has no standard effect. 6-Methylation, however, is generally associated with some degree of instability in the molecular complexes formed, denoting a reduction in the combining capacity normally exhibited by carbostyrils. The effects of secondary factors are therefore more evident in the molecular compounds of these 6-methyl derivatives and to such effects may be attributed the irregularity in complex constitution (e.g., the formation of a 1:2 T.N.E. derivative and a 1:1 molecular picrate by 6-methyl-thio-C.) met with in their investigation.

The molecular compounds shown in Table IV again display a high proportion, eight out of thirteen, of complexes of ternary type. Considering all the molecular compounds prepared in the course of this investigation (Tables I-IV), the high proportion of abnormal derivatives, about 70% (27 out of 39), is striking, and gives further point to the view already established that such abnormal complexes are systematic in their origin.

3. "Mixed" Molecular Compounds.

Molecular complexes containing three different substances are rare and, although such mixed termolecular derivatives have been obtained with quinone and phenols⁽⁷⁶⁾,

the "mixed" complexes of 7 (or 5)-methyl- and 5 (or 7)-methyl-ketotetrahydrocarbazoles described on pp.69-72. appear to be the first recorded examples of polynitro complexes containing three different components. Hryhakowski and Adamis⁽⁷⁷⁾ recently attempted to demonstrate the existence of such termolecular complexes in another group of molecular compounds by examination of phase diagrams, but were unable to do so.

It seems unlikely on the evidence given (pp.69-72) that either the binary or ternary "mixed" complexes obtained from the isomeric 5 (or 7)- and 7 (or 5)-methyl-ketotetrahydrocarbazoles contain these isomeric "aromatic" components in equimolecular proportion; the ternary form cannot therefore be regarded as being composed of one molecule of each isomer united to one molecule of "nitro" component. These derivatives, however, possess a distinct identity, for samples of each prepared from different specimens of the mixed "aromatic" isomers and under different conditions of concentration, etc. were always found to be identical. They therefore appear to contain in their crystal lattice molecules of the two isomers arranged in some regular stable pattern.

Hertel and Römer⁽⁷⁸⁾, on the basis of X-ray crystallographic measurements, suggest a crystal structure for a "3:4" complex of T.N.B. and fluorene in which the

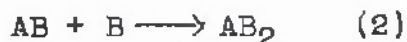
components are arranged in alternating parallel "net-planes". It is possible that those "mixed" derivatives possess a similar crystal structure in which the "aromatic" "net-plane" is composed of molecules of each isomer arranged in some regular stable pattern.

4. General Considerations.

There remains the possibility that the formation of ternary derivatives is due to some prior association of the "aromatic" component in solution, this association itself being dependent on chemical constitution. The following molecular weight determinations of ketotetrahydrocarbazole (K) and its 8-methyl derivative (by the cryoscopic method in benzene) kindly undertaken by Dr. G. Thomson of this University indicate a negative correlation between degree of association and facility in production of crystalline ternary derivatives and therefore render this view unlikely.

Compound	C (g/100 g C_6H_6)		M. (Found)	Formula Weight
K	0.909,	1.22	211.5, 219	185
8-methyl-K	0.883,	1.24	282.4 282.1	199

It is more probable on general grounds that ternary derivatives result from two bimolecular reactions thus:-



than that they are formed by a termolecular reaction. The formation of a 2:3 derivative by T.N.B. and di-benzyl-m-toluidine (vide supra), the formation of both 1:1 and 1:2 dvts of 2-methyl-K and T.N.B., and the isolation of both binary and ternary mixed derivatives from 5 (or 7)-methyl-K. and 7 (or 5)-methyl-K. and picric acid appear to provide factual evidence for this view. These equilibria while normally influenced by the constitutional factor in favour of 1:2 formation will also be affected by secondary factors such as crystalline convenience, complex and component solubility, etc., so that under certain conditions in which the constitutional factor is weakened the binary form may crystallise preferentially and in rare cases both forms may be isolable.

No other property of ternary complexes can be correlated with their abnormal constitution. As illustrated by the complexes of methyl derivatives of K. (Table I), they conform to the same colour and melting point rules as binary derivatives⁽⁹⁾. They are formed by substances which, like K., form an extensive range of derivatives and by substances of limited range, like coumarin and carbostyrl. Their stability may be as great as the most stable binary complexes (complexes of

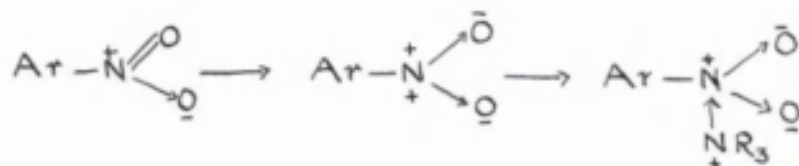
K and its homologues), or may be very low (as in coumarin-T.N.B.⁽⁸⁾, which is only shown on a melting point curve). "Aromatic" substances which yield 1:2 derivatives cannot therefore be regarded as intermediate, in combining capacity towards "nitro" bodies, between substances which yield normal 1:1 derivatives (e.g., naphthalene⁽²⁾) and those which entirely fail to combine (e.g., diphenylmethane⁽⁵⁾).

These facts suggest strongly that ternary complexes are formed by a duplication of the same mechanism by which the components are united in a normal binary complex.

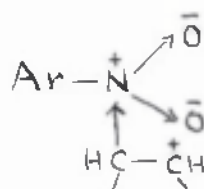
5. The Mechanism of Complex Formation.

There are three current conceptions of the nature of the forces holding the components together in molecular compounds of aromatic polynitro substances.

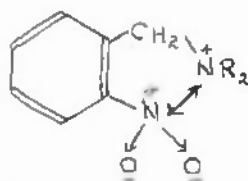
(a) The components are combined by a true covalent bond in which the "nitro" body acts as the acceptor and the "aromatic" component as the donor. This view has been considerably developed by Bennett and his co-workers who originally⁽⁷⁹⁾ postulated that the union of a "nitro" compound with an aromatic amine took place thus:-



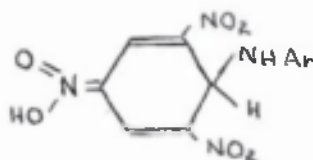
and that to a similar mechanism, in which a suitably polarised ethylene bond in the aromatic ring acted as donor, was due the complexes of aromatic hydrocarbons.



In support of this view they advanced evidence to show that o-nitrobenzylidialkamines show intramolecular coordination.



Recently⁽⁸⁰⁾ Bennett has modified this view and has put forward the following formulation for a complex of a "nitro" body and an aromatic amine



which is identical with that previously suggested by Sudborough⁽⁸¹⁾ but later abandoned by him⁽⁷⁾. A similar formulation for complexes of halogen substituted "nitro" compounds with amines had previously been put forward by Buehler, Hisey and Wood⁽⁸²⁾.

The most convincing evidence yet obtained that a covalent link is involved is provided by Hammick and Sixsmith⁽⁸³⁾ who show that the complex of indene and methyl-4:6:4¹:6¹-tetranitrodiphenate is formed and decomposed at a measurable speed and consequently involves some covalency change. Bamberger and Dimroth⁽¹²⁾, however, maintain that in the formation of a typical polynitro complex like anthracene picrate equilibrium is attained instantaneously and Bennett and Wain⁽⁸⁰⁾ state that in their researches they observed no time factor in the production of colour when the components of a complex were dissolved together. It appears therefore that while the complex investigated by Hammick and Sixsmith may involve electron donation, this is not general.

The evidence against this view that the components are united by a true coordinate link appears to be very strong. A bond of such a definite character is scarcely compatible with the instability of molecular complexes in solution and in the fluid state, nor with the results of this investigation which show that changes in the nature of solvent and concentration, and comparatively slight changes in constitution sometimes effect dramatic changes in complex constitution. Also the researches of Briegleb and Hertel (vide infra) strongly suggest a bond of less definite character.

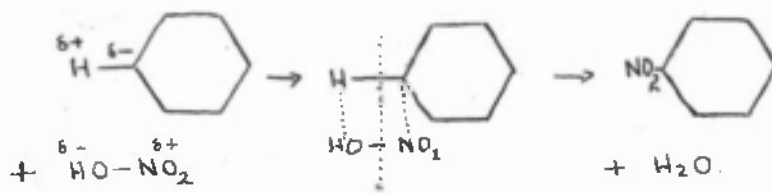
(b) Molecular complexes may be merely crystal-lattice compounds, their composition depending only on considerations of packing. This view can be dismissed as entirely inadequate since it has already been proved that a primary factor in the formation of ternary complexes is constitutional.

(c) The mechanism is in a sense intermediate between those described in (a) and (b) being less stable than a true coordinate link but more definite than mere van der Waal's forces. This view point, which accords best with the properties of these substances and which has received the greatest support, was first definitely stated by Werner⁽⁸⁴⁾ and has been extended by Kremann, Pfeiffer, Brieglieb and others. Although Werner showed that this force, which has been termed "residual valency", "the saturation of residual fields of force", etc., acts between the nitro groups of the "nitro" component and the double bonds of the ring in the "aromatic" component, the exact nature of this force remained obscure until Brieglieb⁽⁸⁵⁾ pointed out that it is most probably an inductive mechanism. The highly polar nitro-groups induce a charge of opposite sign in the polarisable "aromatic" component and the mutual attraction of those opposite charges supplies the force which holds the components

together. This view is in harmony with the known properties of molecular complexes: it agrees with the fact that the introduction of ortho and para directing substituents like OH and NH_2 - which facilitate substitution - i.e., increase the polarisability - increase the tendency of an "aromatic" substance to yield stable molecular derivatives. It is also supported by the recent work of Bennett and Wain⁽⁸⁰⁾ who show that in the "nitro" component the nitro groups can be replaced by other electropolar groups like -CN or -CO.Cl, and is in harmony with the results of X-ray crystallographic examination of molecular complexes obtained by Hertel⁽⁷⁸⁾, (86), (87) and Anderson⁽⁸⁸⁾.

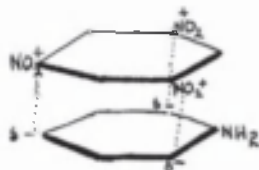
6. Suggestions for the Formation of Ternary Complexes.

According to Ingold⁽⁸⁹⁾, the charges induced in a polarisable aromatic compound by an attacking electropositive group are located at certain points in the benzene ring. The positions at which nitration occurs are regarded as the sites of these small induced negative charges and the ease of nitration gives some indication of the magnitude of these charges. The formation of a transient complex of nitric acid and benzene is supposed to precede nitration thus:-

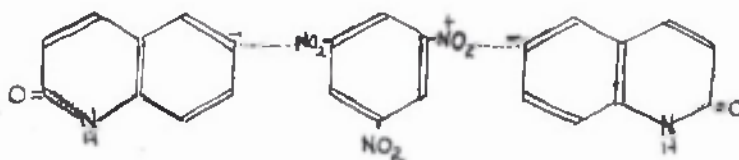


According to Kauffman and Petheou de Petherd⁽⁹⁰⁾ carbostyryl nitrates extraordinarily easily to give only one mono-nitro derivative, the 6-nitro compound. Mears, Oakeshott and Plant⁽³⁶⁾ show that ketotetrahydrocarbazole and its 8-methyl derivative also nitrate in the 6-position whereas the 6-methyl derivative yields on nitration the 7 (or 5)-nitro compound. It would therefore appear that in both carbostyryl and ketotetrahydrocarbazole the negative charge induced by a positive dipole is confined to the 6-position which is the position at which substitution causes a reduction in combining capacity towards "nitro" substances (p. 85).

In simple amines and phenols, which yield particularly stable normal complexes, the induced charges appear on the ring carbon atoms ortho and para to the substituent, and the structure of complexes of such substances with, for instance, trinitrobenzene, is pictured thus:-



The ring planes are parallel and each polar group is at the shortest possible distance from an induced negative charge. This configuration is according to Briegleb⁽⁹¹⁾ most probable, being the position of least free energy. Such a formulation is, however, not practicable for the complexes of substances like carbostyryl and ketotetrahydrocarbazole in which an induced charge of relatively considerable magnitude is located at one point only, and the abnormal composition of the complexes of such substances may be explained by this fact. It seems possible that in such ternary complexes each of the two "aromatic" molecules is bound to one nitro group by the electrostatic attraction existing between that nitro group and the induced negative charge in the 6-position, thus:-



Hertel's researches on the crystal structure of aromatic polynitro substances and the additive complexes which they form have led him to the belief that in the crystal-lattice of "nitro" substances⁽⁹²⁾ and in some cases, (e.g., T.N.B. derivative of anthracene⁽⁷⁸⁾), of their

molecular compounds, the nitro groups of one molecule of the "nitro" component may induce charges on the ring carbon atoms of another. The mutual attraction of these "nitro" molecules serves to orient the whole structure into a series of alternate parallel chains or "net planes", so that alternation of component molecules is found in the direction of only one or two of the three axes. It may be that the nitro group in the ternary complex of say carbostyryl and a trinitro substance which is not directly concerned in the union of the components, has such an orienting function.

The two "aromatic" molecules are regarded as combining separately and there is therefore the possibility of a binary complex being obtained under suitable conditions (see p.88). In such a binary complex the nitro groups not concerned in the union can be imagined to have an orienting effect in the crystal-lattice as suggested above. While substitution at the point at which the induced charge appears reduces combining capacity, it does not necessarily prevent the formation of 1:2 derivatives, although it allows the effect of secondary factors to become more potent. The formation of a 1:2 complex by dibenzyl-p-toluidine although dibenzylaniline nitrates to give dibenzyl-p-nitraniline⁽⁹³⁾, therefore does not seriously lessen the validity of these suggestions.

It is of course admitted that the data available at present is relatively inadequate, and the views put forward can only be regarded as tentative suggestions. Evidence on the nitration of the other "aromatic" components used is lacking and it is impossible at present to forecast the action or extent of the effects of secondary factors. Nevertheless none of the results obtained entirely disprove the feasibility of the formulation suggested for ternary derivatives.

The important result of the work described in this thesis is the conclusive evidence that the range of component-constitution which maintains persistence in ternary (1:2) complex formation is sufficiently wide to demonstrate the systematic nature of such trimolecular compounds. On the other hand this range is sufficiently restricted to explain the previous entire absence of clear factual evidence for the view that such ternary complex formation is a permissible alternative to the formation of the equimolecular type normal to mononuclear aromatic substances, and is not an abnormality conditioned by secondary influences.

Thus any satisfactory elucidation of the long standing and interesting problems presented by polynitro molecular compounds must account for the fact that in the formation of 1:2 complexes the chemical constitution of the components is a necessary though not sufficient factor.

S U M M A R Y.

(a) An attempt has been made with reasonable success to investigate the influence of component-constitution in the formation of a hitherto small class of organic molecular complexes which vary in composition from the normal type.

(b) In the course of this work 72 substances were prepared by the author, 37 of which had not previously been described.

(c) 52 new molecular compounds were prepared, of which 26 were of ternary (1:2) composition.

(d) A crystalline complex of 2:3 composition, which was in the first instance obtained by "cross-seeding", with a crystal of a 1:2 complex, is described.

(e) The first case of the production of alternative 1:1 and 1:2 complexes is given.

(f) The first examples of a new type, three-component "mixed" molecular complexes, were isolated.

(g) It is maintained that the results of this work conclusively prove that ternary (1:2) complexes are systematic in their origin in that they are characteristic of components possessing certain chemical structures, and that they are probably formed by a duplication of the mechanism involved in the formation of the normal binary (1:1) type.

(h) The nature of the valency forces binding the components in polynitro molecular complexes is discussed, and a suggested formulation for 1:2 complexes is given. Additional chemical and physical evidence is, however, required for a complete elucidation of such molecular compounds.

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* This abstract is incorrect. Chakravarti and Venkatasubban performed a Skraup reaction on 3-cyano-4-amino-toluene in the presence of As_2O_5 , not as reported here on "3-cyano-4-nitrotoluene ... in presence of As_2O_3 ."

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